Supplementary Information: Surface Forces generated by the action of electric fields across liquid films

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1   Joule Heating

We consider whether Joule heating could possibly be at the origin of the observed forces with electrolytes. To determine if Joule heating could play a role, we estimated the maximum possible volumetric expansion of the ionic liquid droplet held between the electrodes if all the energy from the applied electric field were converted to heating. We first estimate an upper limit in the induced temperature change ΔT, and then calculate the volumetric expansion for this change in temperature.

To start with, we will assume that the ionic liquid, of dielectric constant ϵ_1, is in a one layer capacitor between the gold electrodes, and that the thickness of the capacitor is uniform and equal to the minimum film thickness, D. The capacitor is held at a voltage V. Later on we will consider the case with mica spacers. The energy per unit area of the one layer capacitor is

$$U^{ES} = \frac{1}{2}CV^2 = \frac{\epsilon_1 V^2}{2D} \tag{1}$$

The total energy in the capacitor is is $U = U^{ES}A$, where A is the surface area of the capacitor. The area of the capacitor is simply the volume of the liquid droplet (approximately 10 μL) divided by the thickness of the film, this is, $A = \mathcal{V}/D$. Now, we need to equate U to the change in enthalpy of the ionic liquid, $\Delta H = c_p \mathcal{V} \rho \Delta T$, where c_p and ρ are the specific heat capacity and density of the ionic liquid, respectively. From this energy balance, we find

$$\Delta T = U/\Delta H = \frac{\epsilon_1 V^2}{2D} \cdot \mathcal{V}/D \cdot (c_p \mathcal{V} \rho)^{-1} = \frac{\epsilon_1 V^2}{2D^2 c_p \rho} \tag{2}$$

Note that the change in temperature is a strong function of the film thickness D; the thinner the film, the higher the energy density within the capacitor. We will assume, as a worst case scenario, a thin film with $D = 1$ μm, and a relative dielectric constant of ϵ_1=15. In our gold experiments, the thickness of the liquid film was always kept above 8 μm. The largest applied voltage in our setup is V=10 V. The specific heat capacity of EMIM-TFSI is c_p=1242 JK^{-1}kg^{-1} [?], and the density of this liquid is $\rho = 1520$ kgm^{-3}. Plugging in numbers

$$\Delta T = \frac{(15 \cdot 8.85 \cdot 10^{-12} \text{ Fm}^{-1})(10 \text{ V})^2}{2(10^{-6} \text{ m})^2(1242 \text{ JK}^{-1}\text{kg}^{-1})(1520 \text{ kgm}^{-3})} = 0.0035 \text{ K} \tag{3}$$

If $D = 10$ μm, then the temperature change is even smaller, 35 μK; this is due to the smaller energy density in the capacitor.

In the mica setup we might get a thinner film, of the order of 100 nm, and so it is worth checking if the temperature change would be more significant. The energy per unit area in this case is is

$$U^{ES} = \frac{1}{2}CV^2 = \frac{V^2}{2(D/\epsilon_1 + T/\epsilon_2)} \tag{4}$$

And so the change in temperature is given by

$$\Delta T = \frac{\epsilon_1 V^2}{2(D/\epsilon_1 + T/\epsilon_2)} \cdot \mathcal{V}/D \cdot (c_p \mathcal{V} \rho)^{-1} = \frac{V^2}{2(D/\epsilon_1 + T/\epsilon_2)Dc_p\rho} \tag{5}$$

Let's say the mica is $T = 1$ μm thick, and that $D = 100$ nm. Plugging in numbers

$$\Delta T = \frac{(8.85 \cdot 10^{-12} \text{ Fm}^{-1})(10 \text{ V})^2}{2(2 \cdot 10^{-6} \text{ m}/8 + 10^{-7} \text{ m}/15)(10^{-7} \text{ m})(1242 \text{ JK}^{-1}\text{kg}^{-1})(1520 \text{ kgm}^{-3})} = 0.0091 \text{ K} \tag{6}$$

So, even in the mica setup with a very thin liquid film, the temperature change of the film is extremely modest.

We finally check the change in volume of the liquid for this temperature change. The isobaric thermal expansivity α_p for EMIM-TFSI is $4.883 \cdot 10^{-4}$ K^{-1}[?]. The fractional change in volume is given by $\Delta V/V = \alpha_p \Delta T$. As an upper limit, we use $\Delta T = 0.01$ K, which gives $\Delta V/V = 4.88 \cdot 10^{-6}$, this is, a negligible change in volume is induced even if all the energy of the electric field is used to heat up the ionic liquid.

2 Electrochemistry

The magnitude of the applied potentials are relatively high compared to the electrochemical windows of the ionic liquids used in this experiments, and one might expect electrochemical reactions if the kinetics were favourable. However, we belive that for our AC experiments, where the electrode polarisation is switched at frequencies much greater than 100 Hz, that there are no redox reactions. Our reasoning is based on several observations:

1. In our experiments with mica spacer layers (e.g. Figure 6) between the electrodes and the electrolyte, there is no possibility of electrochemical reactions because this thick (several micrometre) dielectric layer prevents any current flowing. Since the results with no spacer layers (e.g. Figure 7) are qualitatively identical, with the same trends and timescales, we assume that the main characteristics are not arising from electrochemistry.

2. The AC field experiments are reliably reproducible for the full duration of experiments lasting several days, and with tens of hours of applied AC electric field; the reproducibility implying that there are no irreversible electrochemical processes taking place.

3. Under different conditions of DC field, we can create conditions for electrochemical processes-e.g. oxide deposits and gas evolution- and this gives us confidence that we know the 'signature' of redox processes. With sufficiently high frequency AC fields no such redox reaction products are observed. In fact, at the end of a series of AC measurements, we often decrease the frequency towards DC in order to probe the frequency regimes in which the electrochemistry 'emerges'.

3 Fitting of force evolution in electrolytes

For the data reported in Figure 7, we have fitted the asymptotic shape of the force when the field is on to a single exponential function $F = F_{ss}(1 - \exp{-t/\tau_{ss}})$. An example fit is shown in Figure S1.
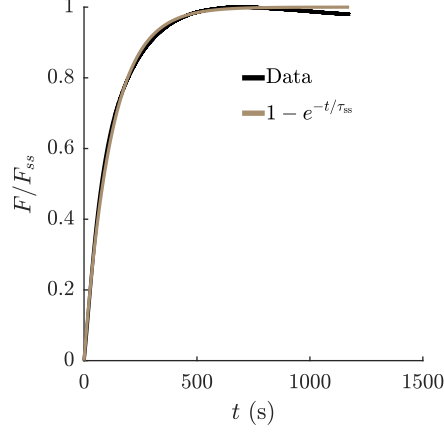
Figure S1: Exponential fit of the slow repulsive response in a experiment with $[C_4C_1Pyrr][NTf_2]$, with $\tau_{ss} = 120$ s. For this example, $V_0 = 7.07$ V, $D_0 = 16.17$ μm, and $\nu_{AC} = 10^3$ s^{-1}.

4 Table of ionic liquid measurements

Ionic liquid	Substrate	T (μm)	D_0 (μm)	V_0 (V)	ν_{AC} (s^{-1})	Sign of F_{ss}
$[C_2C_1Im][NTf_2]$	Mica	2.95	34	3.53, 7.07	10^5	Negative
			45	3.53, 7.07, 9.9	10^5	Negative
$[C_2C_1Im][NTf_2]$	Mica	3.27	0.4, 1.3, 4.2, 16	3.53, 7.07, 9.9	10^4	Negative
$[C_2C_1Im][NTf_2]$	Mica	2.85	0.3, 1.4, 4.3, 16.5	1, 2, 2.82	10^4	Positive
$[C_2C_1Im][NTf_2]$	Gold	0	6.9	7.07	10^4	Negative
			27	3.53, 7.07	10^4	Negative
			42	3.53	10^4	Negative
			42	7.07	$10^4,10^5,10^6$	Negative
$[C_2C_1Im][NTf_2]$	Gold	0	12.73	3.53, 7.07, 9.9	10^4	Negative
			106	9.9	$10^4,10^5,10^6$	Negative
$[C_2C_1Im][NTf_2]$	Gold	0	20	7.07	10^4	Negative
			73.4	7.07	$10^4,10^5$	Negative
$[C_4C_1Pyrr][NTf_2]$	Mica	3.31	0.4	5.45, 7.64	10^4	Negative
				5.92	10^5	Negative
				3.41	10^6	Negative
$[C_4C_1Pyrr][NTf_2]$	Mica	4.34	0.4	4.13, 5.79	10^3	Negative
			1.2	4.13, 5.79	10^3	Negative
			1.2	1.68, 2.36	10^4	Negative
			3.1, 4.5	2.36	10^4	Negative
$[C_4C_1Pyrr][NTf_2]$	Gold	0	8, 10, 12	7.07	10^4	Positive
			16	3.53, 7.07, 9.9	10^4	Positive
			16	7.07	500, 10^3, 5·10^3, 10^5,10^6	Positive
			24	7.07	10^4	Positive
			32	3.53,7.07	10^4	Positive
			48, 64	7.07	10^4	Positive

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References

[1] Hanming Liu, Junhua Huang, and Phillip Pendleton. Experimental and modelling study of CO2 absorption in ionic liquids containing Zn (II) ions. *Energy Procedia*, 4:59–66, 2011.

[2] Javid Safarov, Waleed A El-Awady, Astan Shahverdiyev, and Egon Hassel. Thermodynamic Properties of 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide. *Journal of Chemical & Engineering Data*, 56(1):106–112, 2011.