Supporting Information for

Relating structure and dynamics of ionic liquids under shear by means of reverse non-equilibrium molecular dynamics simulations

Kalil Bernardino,[1*] Mauro C. C. Ribeiro[1]

[1] *Laboratório de Espectroscopia Molecular*, *Departamento de Química Fundamental*,

Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes 748, 05508-000, Brazil

***email: kalil.bernardino@gmail.com**

Contents:

1. Block average results for the viscosity

Table S1. Frequency of momentum swap in RNEMD simulations, resulting shear stress (τ), shear rate ($\dot{\gamma}$), and viscosity (η_{tot}) together with the values of viscosity computed using each one of the equal size blocks of simulations in order to estimate the error bar (η_i values).

Swap	τ (MPa)	$\dot{\gamma}$ (GHz)	η_1 (mPa.s)	η_2 (mPa.s)	η_3 (mPa.s)	η_4 (mPa.s)	η_{tot} (mPa.s)
3-ethyl-1-methyl-imidazolium tetrafluorborate, [EMIM][BF_4]							
5	92.220	39.35	2.331	2.348	2.353	2.343	2.344
10	49.857	10.88	4.634	4.557	4.621	4.524	4.584
16	31.457	5.16	6.249	5.993	6.115	6.023	6.095
20	25.341	3.79	6.720	6.661	6.675	6.678	6.684
40	12.549	1.69	7.918	7.394	7.338	7.159	7.452
50	10.027	1.32	7.660	7.645	7.502	7.486	7.573
80	6.246	0.77	7.794	7.936	9.242	7.848	8.205
100	4.976	0.55	8.168	8.196	9.569	10.841	9.194
3-ethyl-1-methyl-imidazolium dicyanamide, [EMIM][DCA]							
5	94.264	35.25	2.633	2.687	2.681	2.697	2.674
10	50.178	11.62	4.369	4.309	4.294	4.303	4.319
16	31.551	6.37	4.972	4.921	4.962	4.947	4.950
20	25.395	4.93	5.210	5.122	5.209	5.071	5.153
32	15.613	2.99	5.245	5.221	5.210	5.196	5.218
40	12.567	2.39	5.435	5.020	5.308	5.251	5.254
50	10.038	1.88	5.432	5.128	5.454	5.365	5.345
100	4.999	0.91	5.126	5.513	6.095	5.305	5.510
3-ethyl-1-methyl-imidazolium bis(trifluoromethylsulfonyl)imide, [EMIM][NTf_2]							
5	61.716	21.14	2.911	2.912	2.945	2.908	2.919
10	33.182	6.59	5.037	5.152	4.907	4.898	4.998
16	20.933	3.42	6.121	6.000	5.964	6.047	6.033
20	16.857	2.69	6.274	6.460	6.586	6.245	6.391
40	8.373	1.18	7.107	6.892	6.862	6.459	6.852
50	6.689	0.92	7.271	7.502	7.007	7.325	7.276
80	4.168	0.58	7.192	6.850	8.448	6.848	7.334
100	3.321	0.42	7.862	7.712	6.561	6.359	7.123

2. Viscous heat produced by the shear

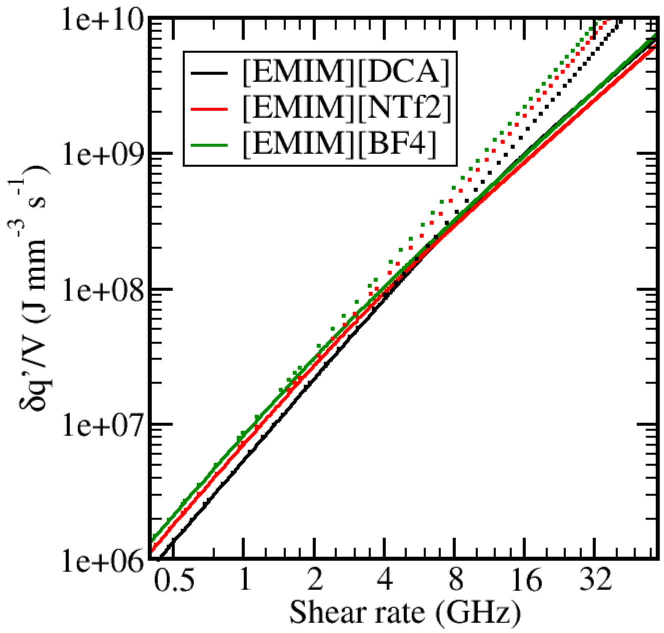

Figure S1 – Rate of heat produced by the non-equlibrium flow by unit of volume at each shear rate. Solid curves: Results computed from the Carreau equation (Equation 2) with fitted parameters for each IL. Dotted curves: Expected behavior if each liquid behaves as newtonian fluid (constant viscosity equal to calculated zero shear viscosities from Carreau Equation, see Table 1 and Figure 3 on the manuscript).

3. Additional radial distribution functions, g(r)

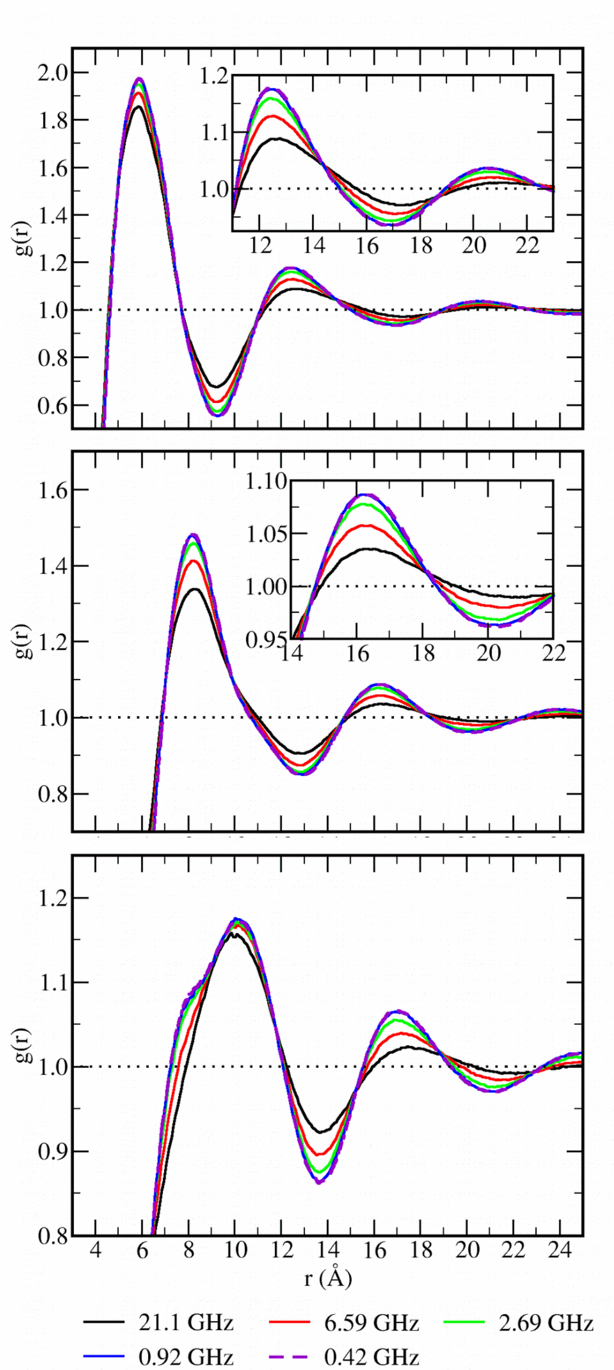

Figure S2. Radial pair distribution function between cation-anion, anion-anion and cation-cation for [EMIM][NTf2] at different shear rates. The insets zoom in the region of second and third coordination shells.

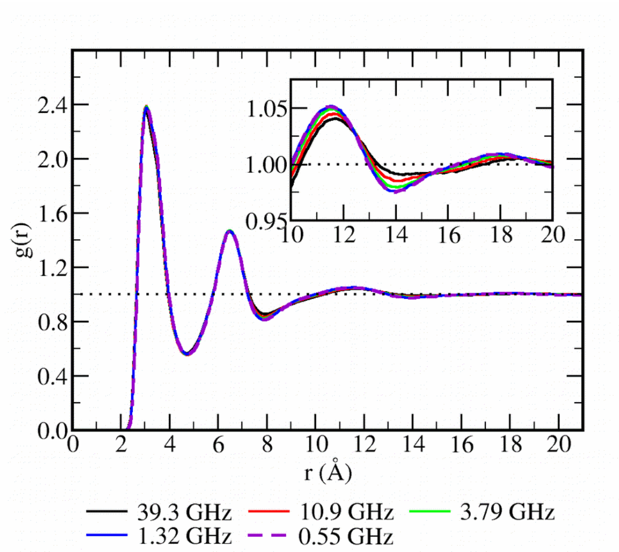

Figure S3. Radial pair distribution function between the hydrogen atom bonded to the carbon 2 of the imidazolium ring and the boron atom of the anion in the [EMIM][BF4] at different shear rates.

4. Correlation between Carreau equation parameters

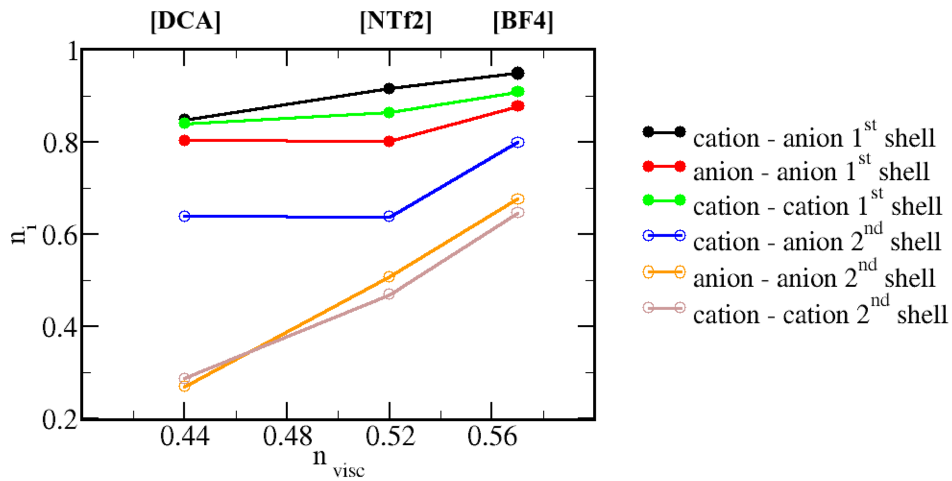

Figure S4. Values of the power-law parameter n_i of Carreau equation used to describe changes in the radial distribution function (Equation 6) against the values for the same parameter that gives the best fit for the viscosity. The anions of each liquid are indicated on the top.

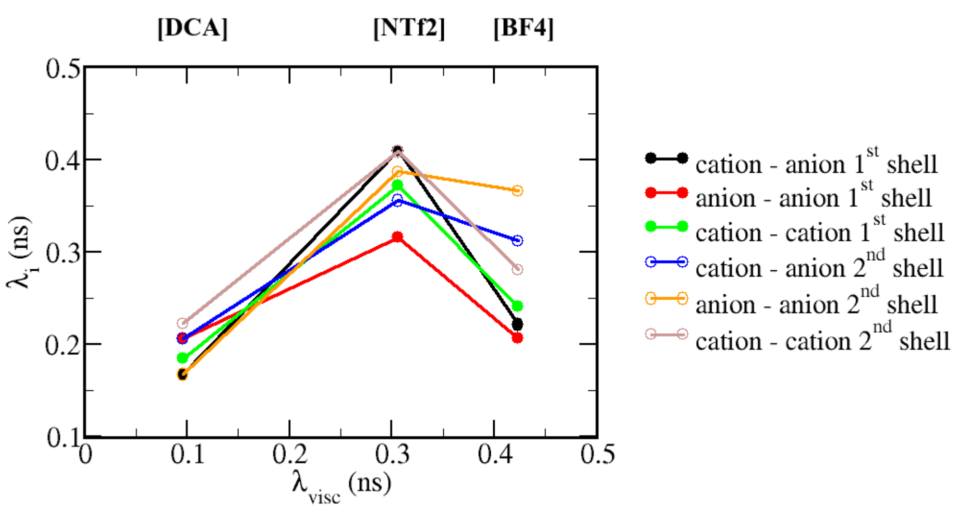

Figure S5. Values of the power-law parameter n_i of Carreau equation used to describe changes in the radial distribution function (Equation 6) against the values for the same parameter that gives the best fit for the viscosity. The anions of each liquid are indicated on the top.

5. Additional spatial distribution functions, sdf

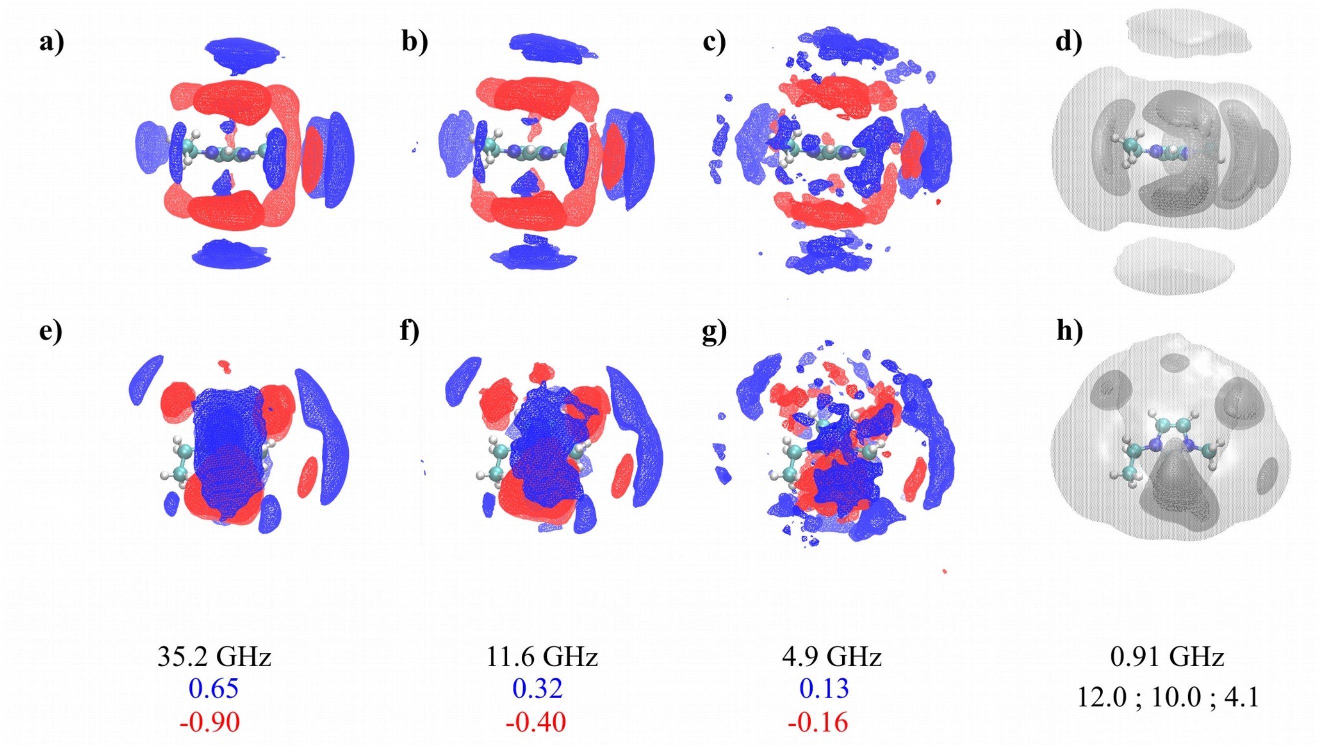

Figure S6. a, b, c, e, f, g: Difference between the sdf of the anion around the imidazolium cation in the [EMIM][DCA] liquid submitted to the shear rates of 35.2 GHz (**a** and **e**), 11.6 GHz (**b** and **f**) or 4.9 GHz (**c** and **g**) and the sdf of the liquid under shear rate of 0.91 GHz. The red isosurfaces indicate decrease of the anion density under higher shear rate, whilst blue isosurfaces correspond to the regions where the density increases with the shear rate. **d** and **h:** sdf of the anion around the cation in the shear rate of 0.91 GHz. Isovalues in nm^{-3} are given at the bottom of the figure.

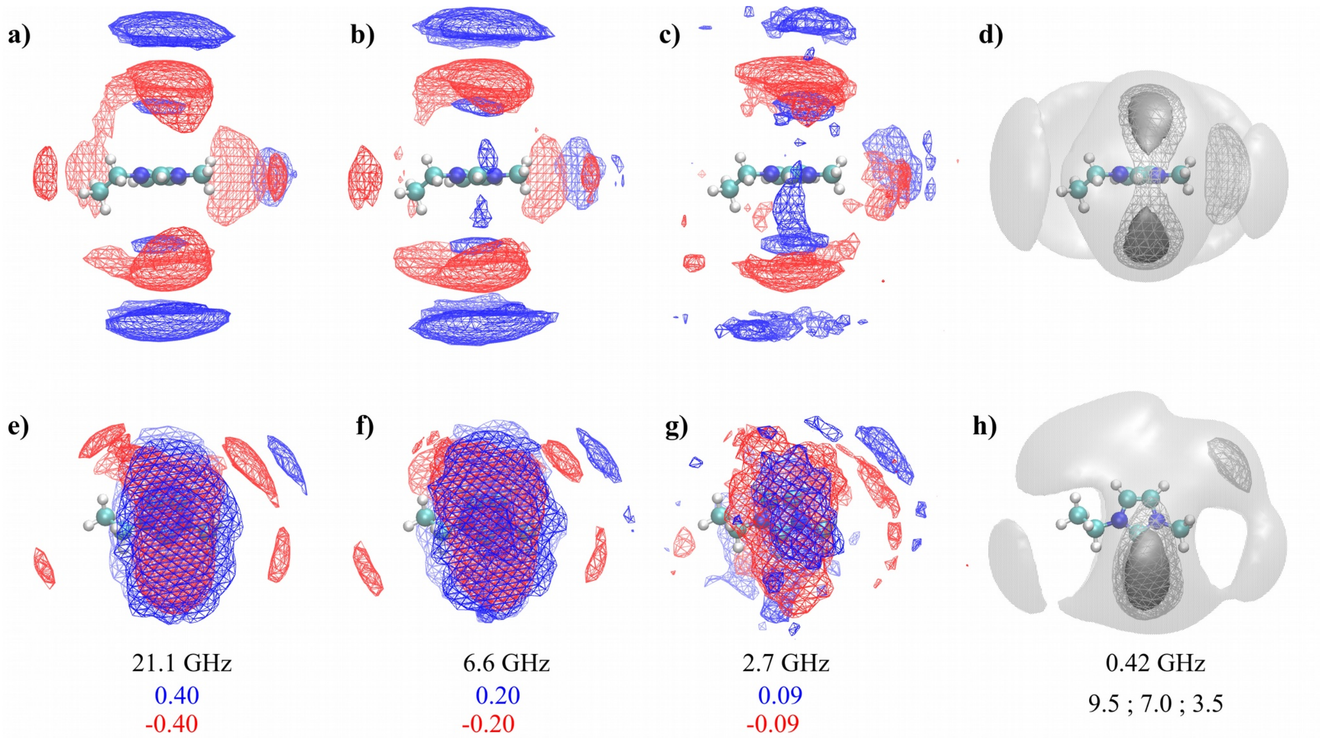

Figure S7. a, b, c, e, f, g: Difference between the sdf of the anion around the imidazolium cation in the [EMIM][NTf2] liquid submitted to the shear rates of 21.1 GHz (**a** and **e**), 6.6 GHz (**b** and **f**) or 2.7 GHz (**c** and **g**) and the sdf of the liquid under shear rate of 0.42 GHz. The red isosurfaces indicate decrease of the anion density under higher shear rate, whilst blue isosurfaces correspond to the regions where the density increases with the shear rate. **d** and **h:** sdf of the anion around the cation in the shear rate of 0.42 GHz. Isovalues in nm^{-3} are given at the bottom of the figure.

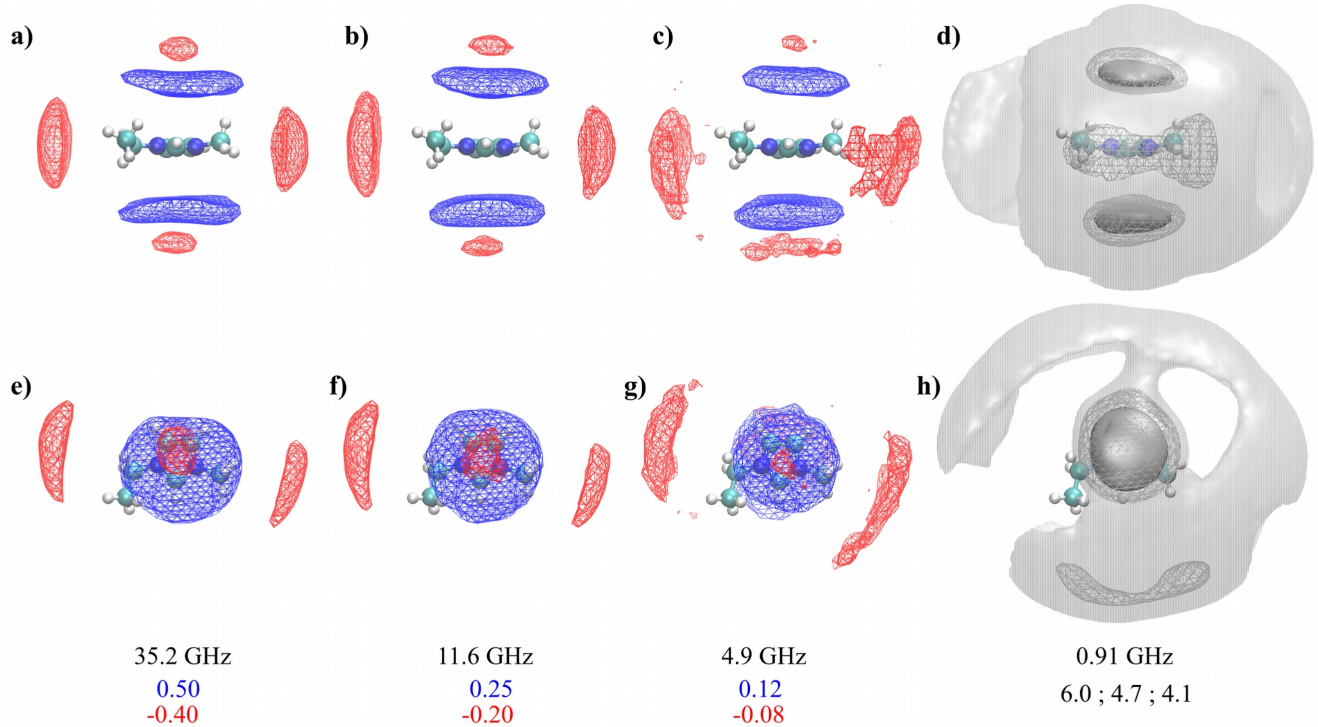

Figure S8. a, b, c, e, f, g: Difference between the sdf of the imidazolium rings around the reference cation in the [EMIM][DCA] liquid submitted to the shear rates of 35.2 GHz (**a** and **e**), 11.6 GHz (**b** and **f**) or 4.9 GHz (**c** and **g**) and the sdf of the liquid under shear rate of 0.91 GHz. The red isosurfaces indicates decrease of the imidazolium density under higher shear rate whilst blue isosurfaces correspond to the regions where the density increases with the shear rate. **d** and **h:** sdf of the anion around the cation in the shear rate of 0.91 GHz. Isovalues in nm^{-3} are given at the bottom of the figure.

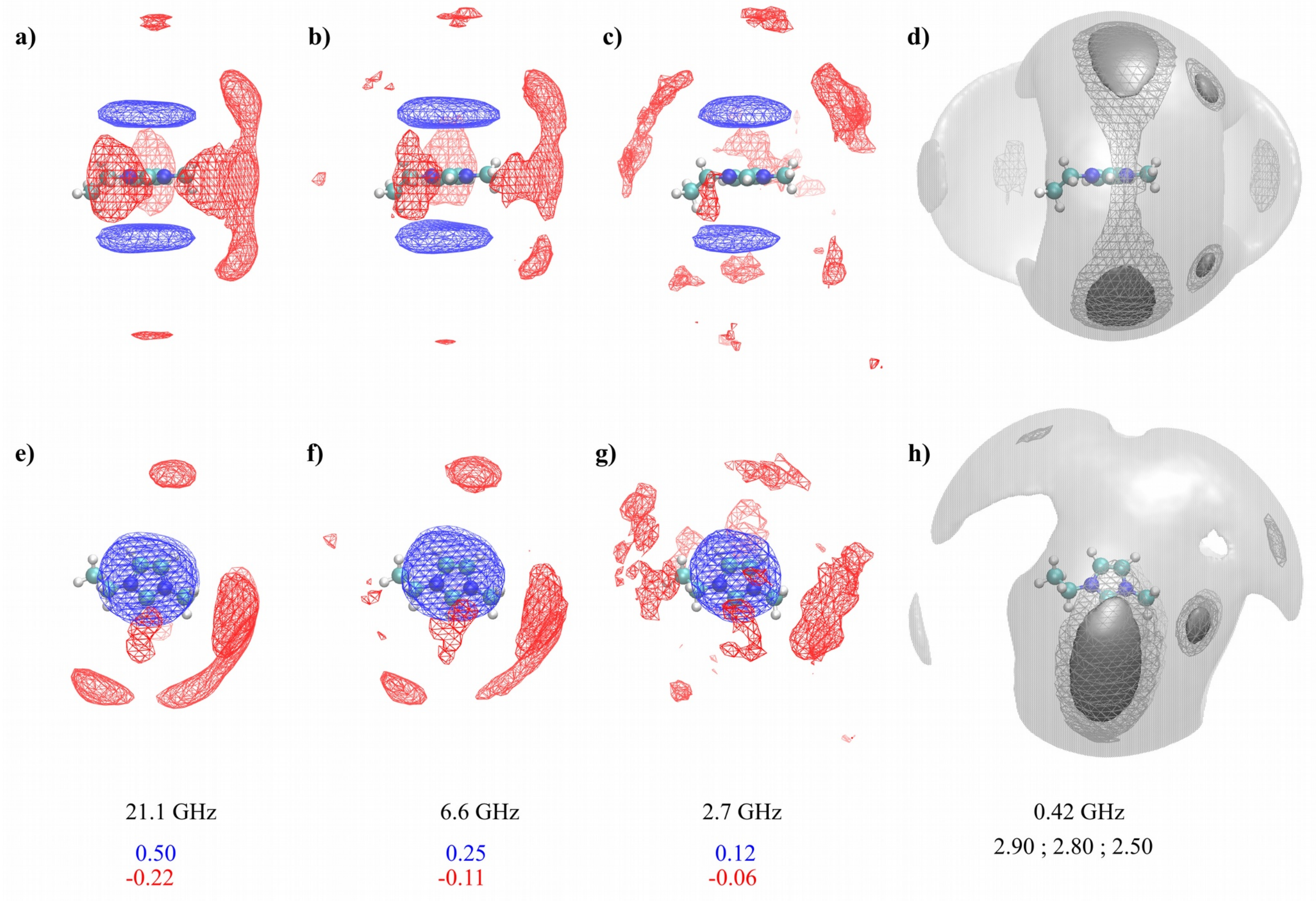

Figure S9 – a, b, c, e, f, g) Difference between the sdf of the imidazolium rings around the reference cation in the [EMIM][NTf2] liquid submitted to the shear rates of 21.1 GHz (**a** and **e**), 6.6 GHz (**b** and **f**) or 2.7 GHz (**c** and **g**) and the sdf of the liquid under shear rate of 0.42 GHz. The red isosurfaces indicate decrease of the imidazolium density under higher shear rate whilst blue isosurfaces correspond to the regions where the density increases with the shear rate. **d** and **h:** sdf of the anion around the cation in the shear rate of 0.42 GHz. Isovalues in nm^{-3} are given at the bottom of the figure.

6. Imidazolium ring orientation

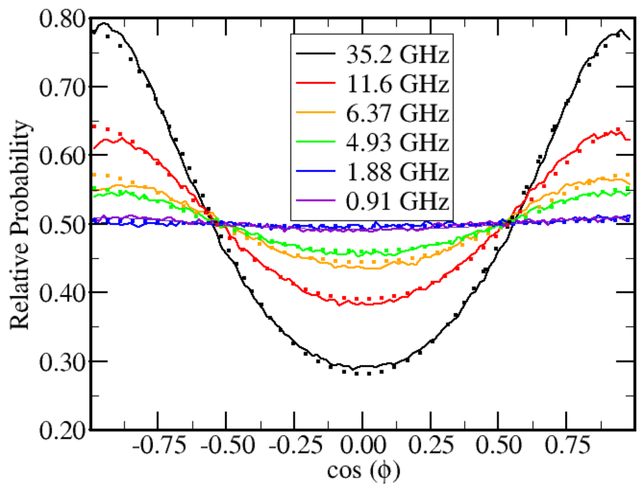

Figure S10. Orientation distribution of the imidazolium ring in the [EMIM][DCA] at several shear rates (solid lines represent simulation data and the corresponding dotted lines represent the fit with Equation 7).

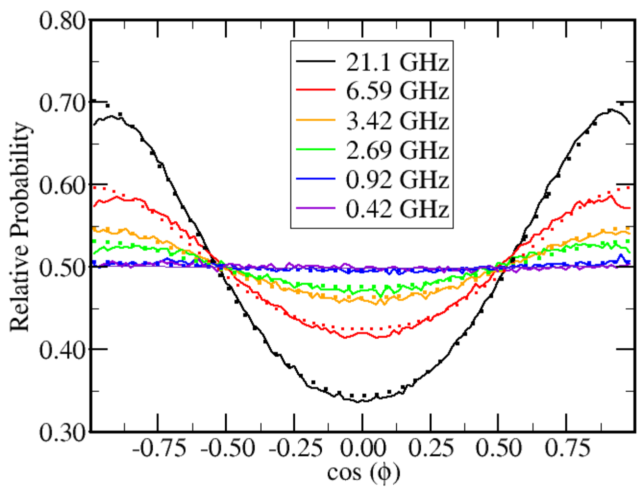

Figure S11. Orientation distribution of the imidazolion ring the [EMIM][NTf2] at several shear rates (solid lines represent simulation data and the corresponding dotted lines represent the fit with Equation 7).

7. Anion orientation

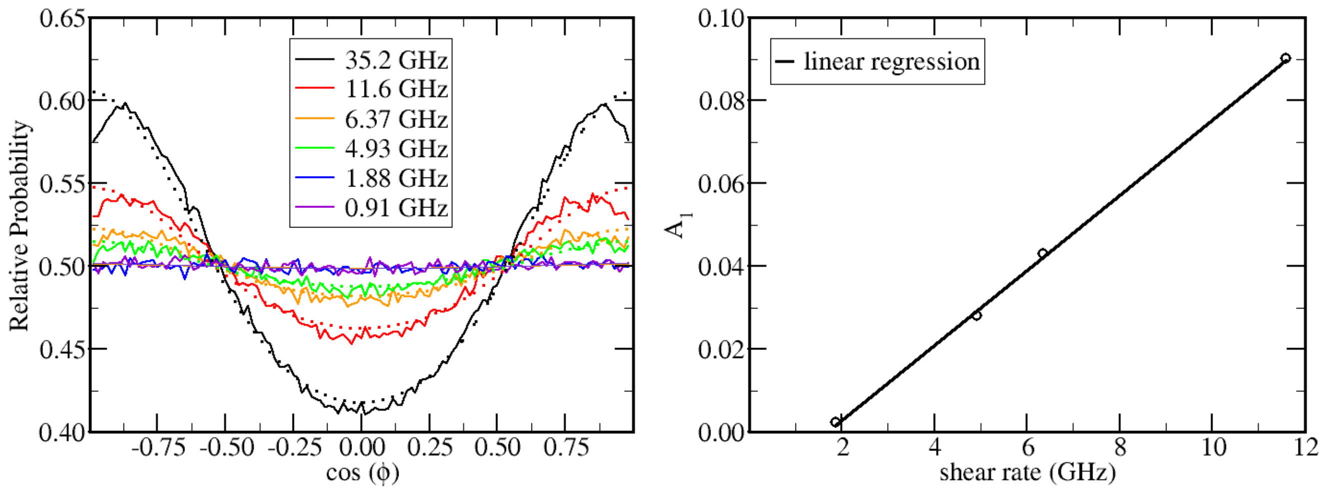

Figure S12. Left: Distribution of the angle ϕ between the vector normal to the plane of the DCA anion and the gradient of velocity at several shear rates. Dotted lines represent the fit using Equation 7. Right: variation of the parameter A_1 in Equation 6 with the shear rate for DCA.

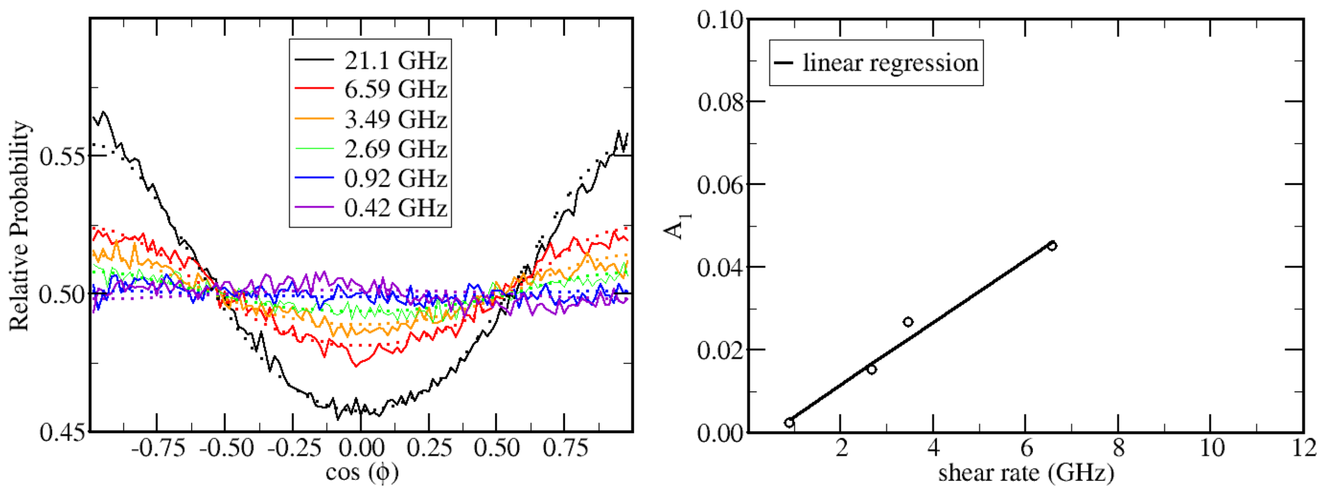

Figure S13 – Left: Distribution of the angle ϕ between the vector normal to the plane of defined by the C and N atoms of NTf2 anion and the gradient of velocity at several shear rates. Dotted lines represent the fit using Equation 7. Right: variation of the parameter A_1 in Equation 6 with the shear rate for NTf2.