Supplementary data

Validity of the Onsager-Glarum Relation in a Molecular Coulomb Fluid: Investigation via Temperature-dependent Molecular Dynamics Simulations of a Representative Ionic Liquid, [BMIM][PF$_6$]

Tamisra Pal[#], Suman Das[#], Dhrubajyoti Maji and Ranjit Biswas[*]

Department of Chemical, Biological and Macromolecular Sciences, S. N. Bose National Centre for Basic Sciences, JD Block, Sector III, Salt Lake, Kolkata 700106, India

[#]Contributed equally to this work

[*]Corresponding Author: Ranjit Biswas, Email: ranjit@bose.res.in; FAX: 91 33 2335 3477

Table S1 Force field parameters of $[BMIM]^+$ and $[PF_6]^-$ are given below:

Lennard-Jones Parameters for different atoms of $[BMIM]^+$ and $[PF_6]^-$

Atom	ε_{ij} (kJ/mol)	σ_{ij} (Å)
CR	0.292	3.55
NA (NAA, NAM)	0.711	3.25
CW (CWA, CWM)	0.292	3.55
H4(H4A, H4M)	0.125	1.72
H5	0.125	1.72
CT (CTM, CT1, CT2, CT3, CT4)	0.276	3.50
H1 (H1M, H2M, H3M, H11, H12)	0.125	1.92
HC (H21, H22, H31, H32, H41, H42, H43)	0.125	2.50
P	0.836	3.94
F	0.255	3.118

Partial charges on each atom of [BMIM]$^+$ and [PF$_6$]$^-$

Atom	$q_i(e)$
CR	0.060
NA (NAA, NAM)	0.052
CW (CWA, CWM)	-0.020
H4(H4A, H4M)	0.096
H5	0.096
CTM, CT1	-0.089
CT2, CT3	-0.038
CT4	-0.065
H1 (H1M, H2M, H3M, H11, H12)	0.105
HC (H21, H22, H31, H32, H41, H42, H43)	0.026
P	0.580
F	-0.230

Bond lengths and bond force constants for $[BMIM]^+$ and $[PF_6]^-$

Bonds	r_0 (Å)	K_b (kJmol^{-1}Å^2)
CR/CW-H5/H4	1.08	Constrained
CT-H1/HC	1.09	Constrained
CR-NA	1.315	1996
CW-NA	1.378	1787
CW-CW	1.341	2176
NA-CTM/CT1	1.466	1410
CT-CT	1.529	1121
P-F	1.6	1673

Angles and corresponding angle force constants for [BMIM]$^+$ and [PF$_6$]$^-$

Angles	θ_0 (deg)	K_θ (kJmol^{-1}rad^2)
CW-NA-CR	108.0	292.6
CW-NA-CTM/CT1	125.6	292.6
CR-NA-CTM/CT1	126.4	292.6
NA-CR-H4/H5	125.1	146.3
NA-CR-NA	109.8	292.6
NA-CW-CW	107.1	292.6
NA-CW-H5/H4	122.0	146.3
CW-CW-H4/H5	130.9	146.3
NA/CT-CT-H1/HC	110.7	156.6
NA/CT-CT-CT	112.7	418.4
H1/HC-CT-H1/HC	107.8	138.1
F-P-F	90.0	836.8

Coefficient of Fourier series of various dihedrals for [BMIM]$^+$

Dihedrals	V_1 (kJ/mol)	V_2 (kJ/mol)	V_3 (kJ/mol)
X^a-NA-CR-X	0	19.46	0
X-CW-CW-X	0	44.98	0
X-NA-CW-X	0	12.55	0
CW-NA-CTM/CT1-H1	0	0	0.519
CR-NA-CTM/CT1-H1	0	0	0
CW-NA-CTM/CT1-C2	-7.154	4.43	0.877
CR-NA-CTM/CT1-C2	-5.269	0	0
NA-CTM/CT1-CT2-CT3/CT4	-7.480	-0.681	1.02
NA-CTM/CT1-CT2-HC	0	0	0
CT-CT-CT-H1/HC	0	0	1.531
H1/HC-CT-CT-H1/HC	0	0	1.331
CT-CT-CT-CT	7.28	-0.657	1.167
X-NA-X-X	0	8.37	0
X-CR/CW-X-X	0	9.2	0

^{a}X represents improper dihedral

The force field parameters of [BMIM]⁺is adopted from the following paper: J. N. Canongia Lopes, J. Deschamps, and A. A. H. Padua, J. Phys. Chem. B **108,** 2038 (2004). Several modifications of the force field parameters, performed by J. N. Canongia Lopes, J. Deschamps, and A. A. H. Padua, J. Phys. Chem. B **108,** 11250 (2004) has also been considered. The force field parameters of [PF$_6$]⁻ is taken from: O. Borodin, G. D. Smith, and R. L. Jaffe, J. Comput. Chem. **22,** 641 (2001). The total charge of both the cation and anion as well as some of the Lennard-Jones parameters is modified following the work of B. L. Bhargava and S. Balasubramanian, J. Chem. Phys. **127,** 114510 (2007).
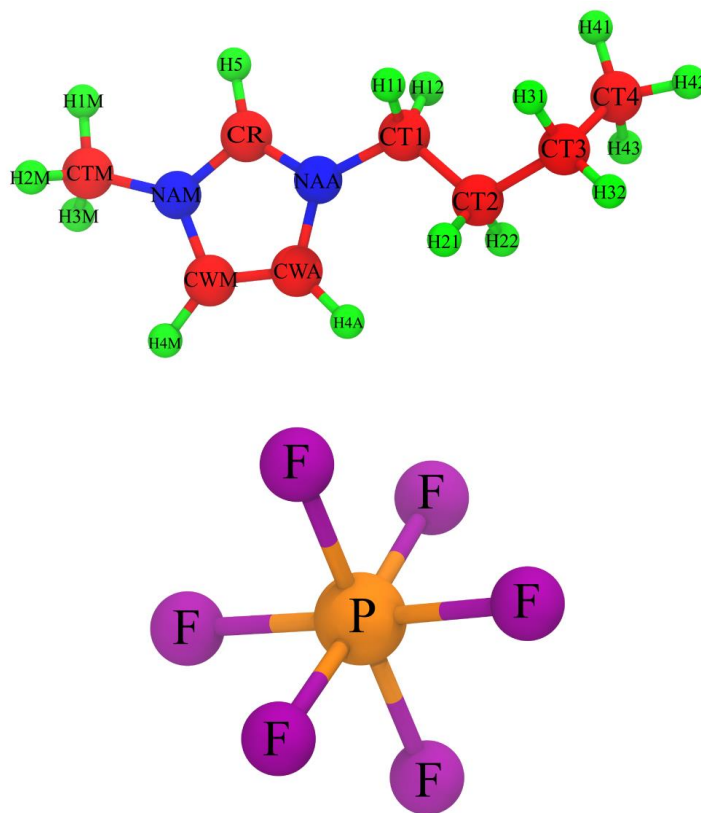

Fig. S1. Representations of [BMIM]⁺ and [PF$_6$]⁻ in our simulations with various atom types.

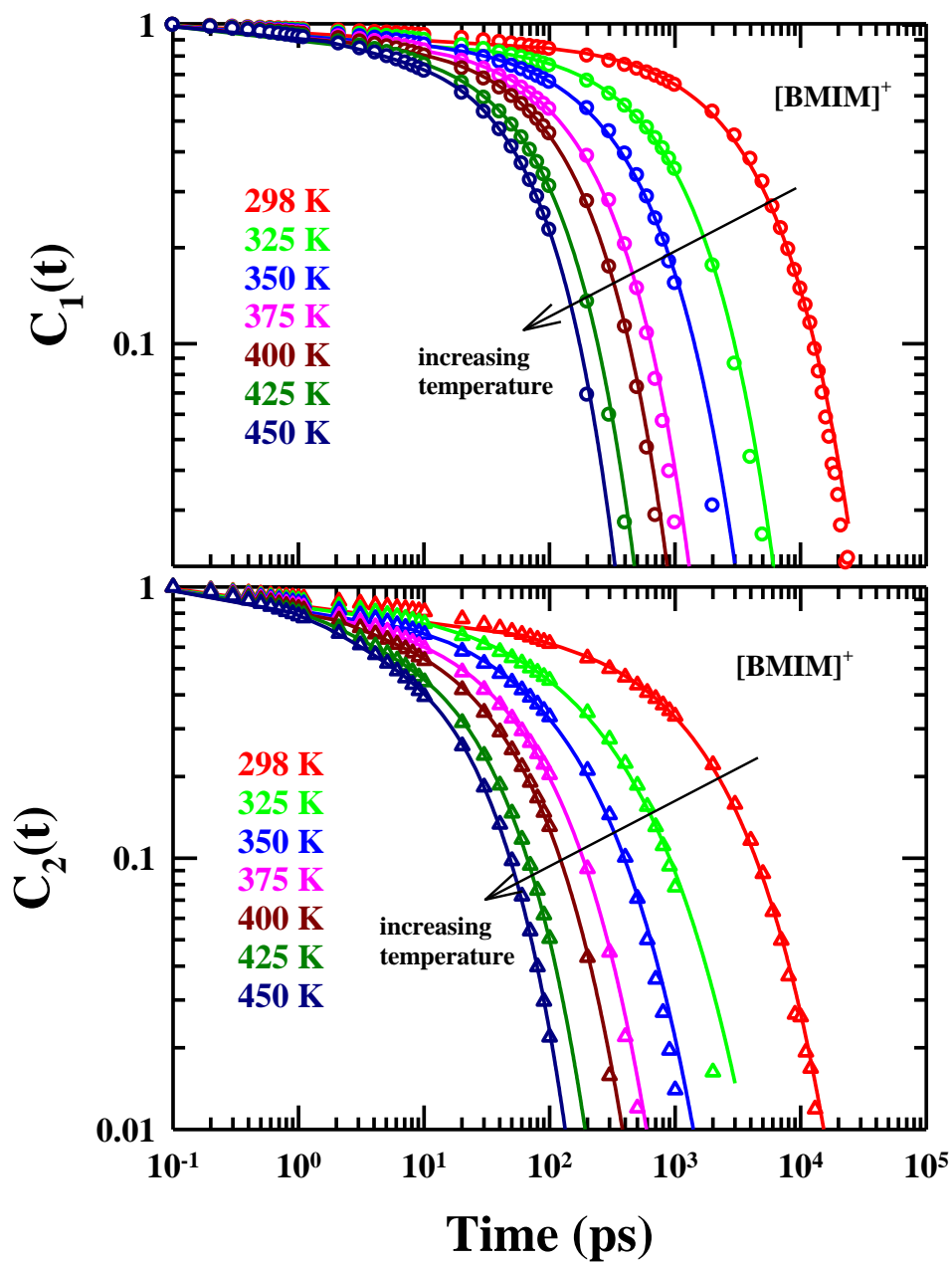**Fig. S2.** Reorientational correlation function, $C_l(t)$ of [BMIM]$^+$ cation for all the temperatures. The upper panel shows the data for rank 1 ($l = 1$), and the lower panel for rank 2 ($l = 2$). The simulated data for each temperature is shown by markers and the continuous lines represent the stretched exponential fitting. The fitting parameters are shown in Table S2.

Table S2 Stretched-exponential fitting parameters for reorientational correlation functions, $C_1(t)$ and $C_2(t)$ of [BMIM]$^+$at various temperatures

Temperature (K)		a_1	τ_1(ps)	a_2	τ_2(ps)	a_3	τ_3 (ps)	β	$\langle\tau\rangle^*$ ps
298	$C_1(t)$	0.1	8.7	0.9	4565.0	-	-	0.75	4892.0
	$C_2(t)$	0.11	0.9	0.15	29.0	0.74	1390.0	0.61	1520.0
325	$C_1(t)$	0.1	5.7	0.9	1078.0	-	-	0.77	1132.0
	$C_2(t)$	0.09	1.3	0.91	196.0	-	-	0.52	332.0
350	$C_1(t)$	0.08	2.5	0.92	479.0	-	-	0.73	537.0
	$C_2(t)$	0.12	1.4	0.88	101.0	-	-	0.57	143.0
375	$C_1(t)$	0.09	2.0	0.91	233.0	-	-	0.78	245.0
	$C_2(t)$	0.15	1.4	0.85	54.9	-	-	0.63	66.3
400	$C_1(t)$	0.09	1.9	0.91	158.0	-	-	0.79	165.0
	$C_2(t)$	0.17	1.4	0.83	37.6	-	-	0.64	43.6
425	$C_1(t)$	0.11	1.8	0.89	93.1	-	-	0.82	92.5
	$C_2(t)$	0.21	1.4	0.79	23.7	-	-	0.70	24.0
450	$C_1(t)$	0.13	1.8	0.87	70.2	-	-	0.85	66.7
	$C_2(t)$	0.25	1.3	0.75	19.0	-	-	0.75	17.3

$*\langle\tau\rangle = a_1 \times \tau_1 + a_2 \times \tau_2 + a_3 \times \left(\frac{\tau_3}{\beta}\right) \times \Gamma\left(\frac{1}{\beta}\right)$ for $C_2(t)$ at 298 K otherwise $\langle\tau\rangle = a_1 \times \tau_1 + a_2 \times \left(\frac{\tau_2}{\beta}\right) \times \Gamma\left(\frac{1}{\beta}\right)$
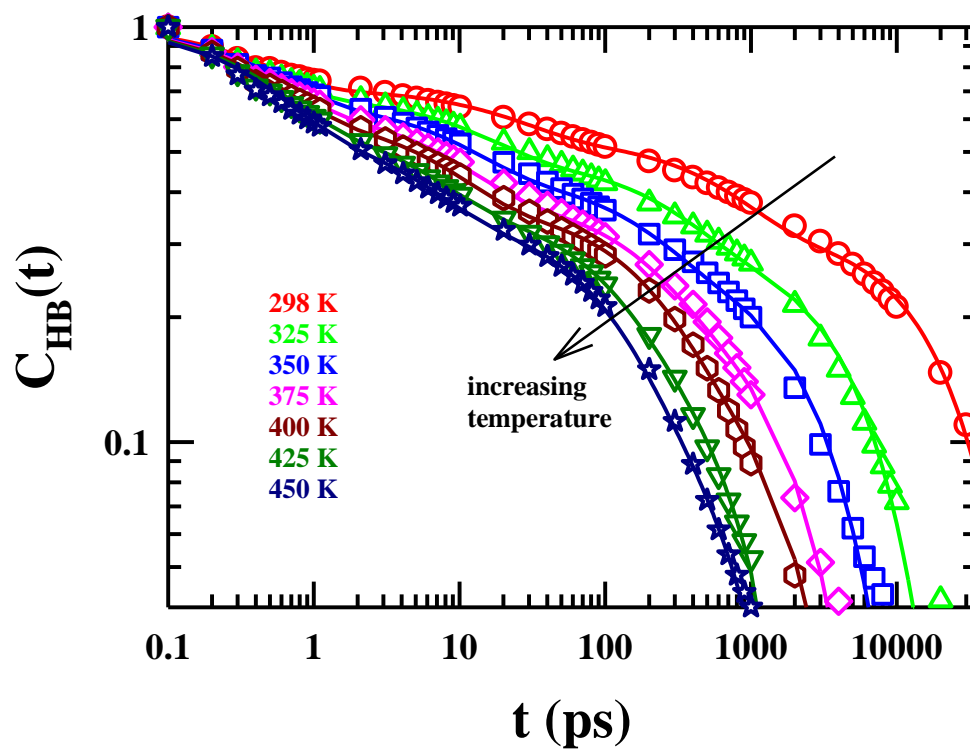
Fig. S3. Structural hydrogen bond correlation function, $C_{HB}(t)$ across all the temperatures with multi-exponential fittings. Simulated values are shown using different markers at every temperature and continuous lines represent corresponding fittings. The fitting parameters are shown in Table 4 of the main text.