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Pressure-responsive mesoscopic structure in room temperature ionic liquids

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Supplementary Information.

Computational details.

All of the simulations were made using the DL-POLY 2 package [1] for 460 ion pairs $[C_8mim][BF_4]$. Canongia Lopes and coworkers [2] and Liu and others [3] intra- and interatomic interaction parameters have been used for the cation and the anion, respectively.

Initial configurations were created using PACKMOL[4] at low density. All the systems were thoroughly equilibrated: care was paid that the calculated structural properties were not depending on the particular simulation trajectory chosen and we verified that the S(Q) was not changing when independent simulation trajectories starting from different initial conditions were considered. Eventually Leapfrog algorithm was used for integration of the equations of motion (1fs step) at 320 K and various pressures in the NPT Hoover ensemble. Parameters for the NPT Hoover thermostat and barostat relaxation time were 0.03 and 0.7 ps respectively.

After equilibration, all trajectories were subsequently run for 5 ns, and the last one ns of the equilibrated trajectory was used for further analysis of structural properties. Calculation procedures for total structure factor functions and their components followed methods described in a well-documented literature. [5–8]

Structural observables have been obtained using the TRAVIS package[9].

Calculated equilibrium values for the densities at 320 K are reported in Table 1.

P (atm)	ρ (g/cc)	Box size (Å)
1	1.0721	58.58
300	1.0843	58.36
1000	1.1063	57.97
3000	1.1583	57.09
9900	1.2560	55.57

1 I. T. Todorov, W. Smith and M. T. Dove, *J. Mater. Chem.*, 2006, **16**, 1911–1918.

2 J. N. Canongia Lopes, J. Deschamps and A. A. H. Padua, *J. Phys. Chem. B*, 2004, **108**, 2038–2047.

3 Z. Liu, S. Huang and W. Wang, *J. Phys. Chem. B*, 2004, **108**, 12978–12989.

4 L. Martínez, R. Andrade, E. G. Birgin and J. M. Martínez, *J. Comput. Chem.*, 2009, **30**, 2157–2164.

5 C. S. Santos, H. V. R. Annapureddy, N. S. Murthy, H. K. Kashyap, E. W. Castner and C. J. Margulis, *J. Chem. Phys.*, 2011, **134**, 064501.

6 H. K. Kashyap, C. S. Santos, H. V. R. Annapureddy, N. S. Murthy, C. J. Margulis and E. W. Castner, *Faraday Discuss.*, 2012, **154**, 133 – 143.

7 H. V. R. Annapureddy, H. K. Kashyap, P. M. De Biase and C. J. Margulis, *J. Phys. Chem. B*, 2010, **114**, 16838–16846.

8 H. K. Kashyap, J. J. Hettige, H. V. R. Annapureddy and C. J. Margulis, *Chem. Commun.*, 2012, **48**, 5103–5.

9 M. Brehm and B. Kirchner, *J. Chem. Inf. Model.*, 2011, **51**, 2007–23.

Additional Figures

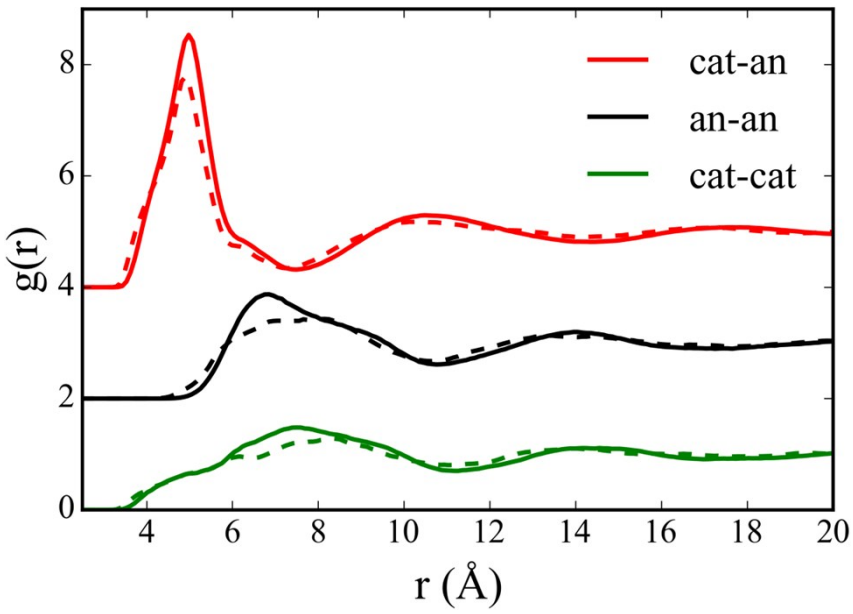

Figure S1. Pair correlation functions between ionic species center of masses (CM for the imidazolium cation and the Boron atom for the anion). The two extremes cases of 1 (continuous line) and 10,000 (dashed line) atm are compared at 320 K. Red, black and dark green curves refer to cation-anion, anion-anion and cation-cation correlations, respectively. Data are vertically shifted for clarity.

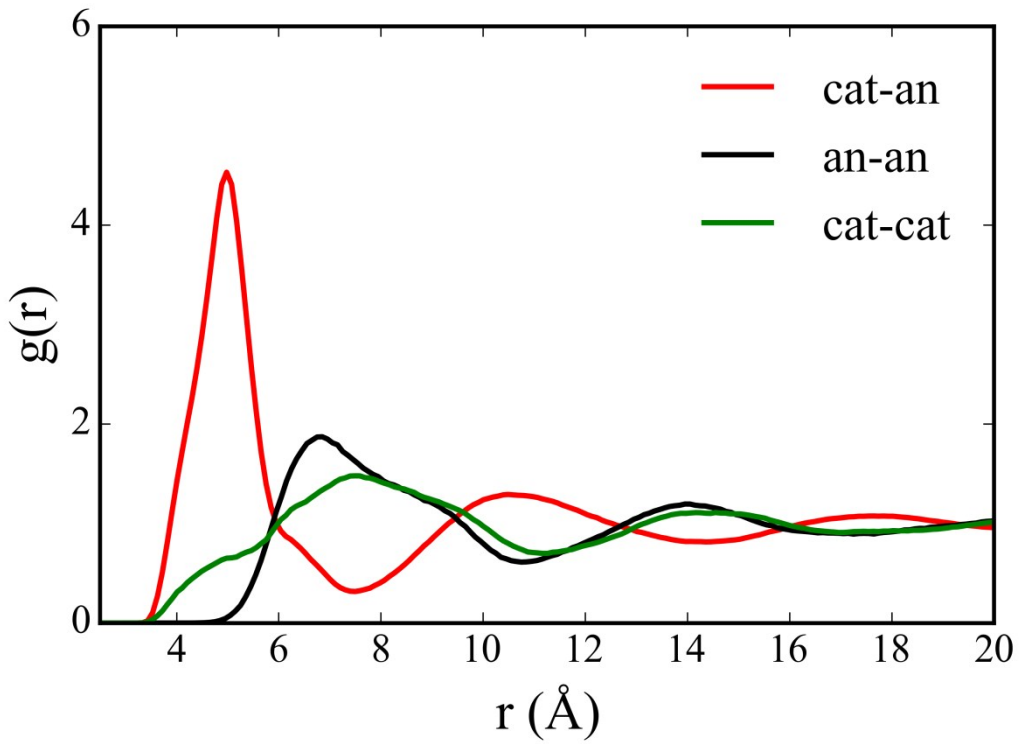

Figure S2. Pair correlation functions between ionic species center of masses (CM for the imidazolium cation and the Boron atom for the anion) at 1 atm and 320 K. Red, black and dark green curves refer to cation-anion, anion-anion and cation-cation correlations, respectively. This figure allows visualizing the onion-like structure of the charged moieties correlations, where the out of phase character between the cat-an and the an-an or cat-cat pdfs becomes evident.

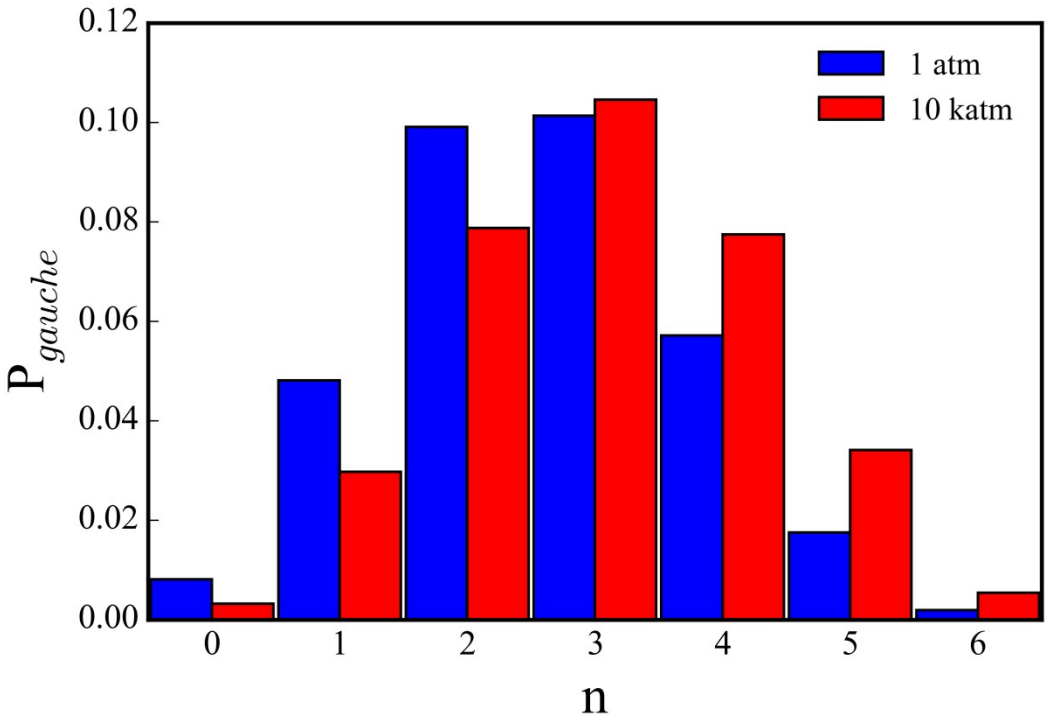

Figure S3. The fraction of the number of gauche conformers along a given octyl chain (where six dyhedrals are defined) is reported for the two extreme pressures (1 (blue) and 10,000 (red) atm respectively).

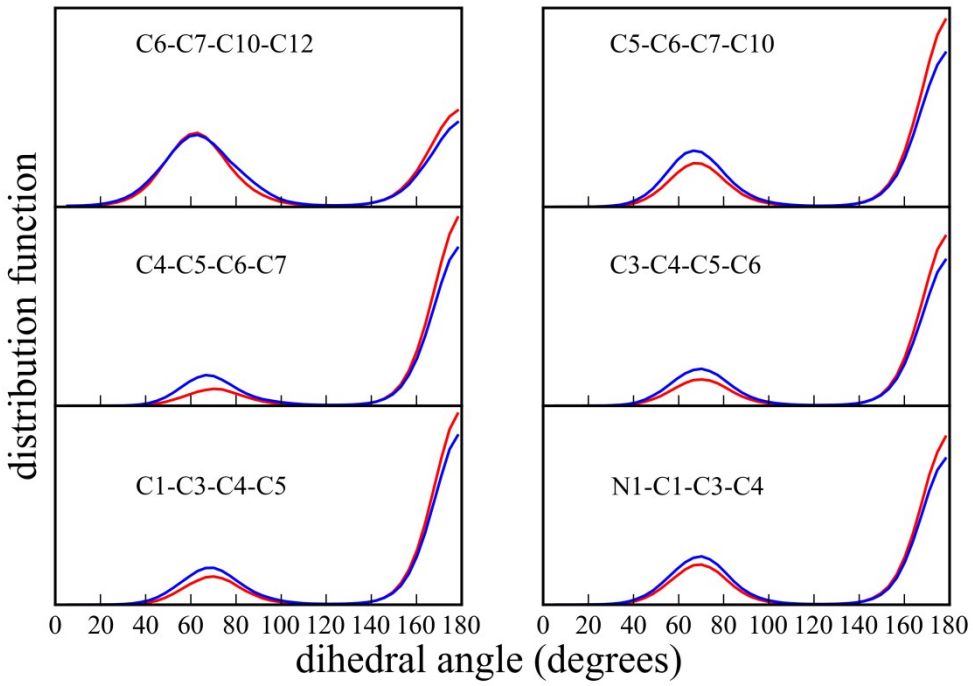

Figure S4. Dihedral distribution functions along the octyl side chains (where six dyhedrals are defined) is reported for the two extreme pressures (1 (red) and 10,000 (blue) atm respectively). The atomic sequence along the octyl chain is: N1-C1-C2-C3-C4-C5-C6-C7-10-C12, where C12 is the terminal methyl group.

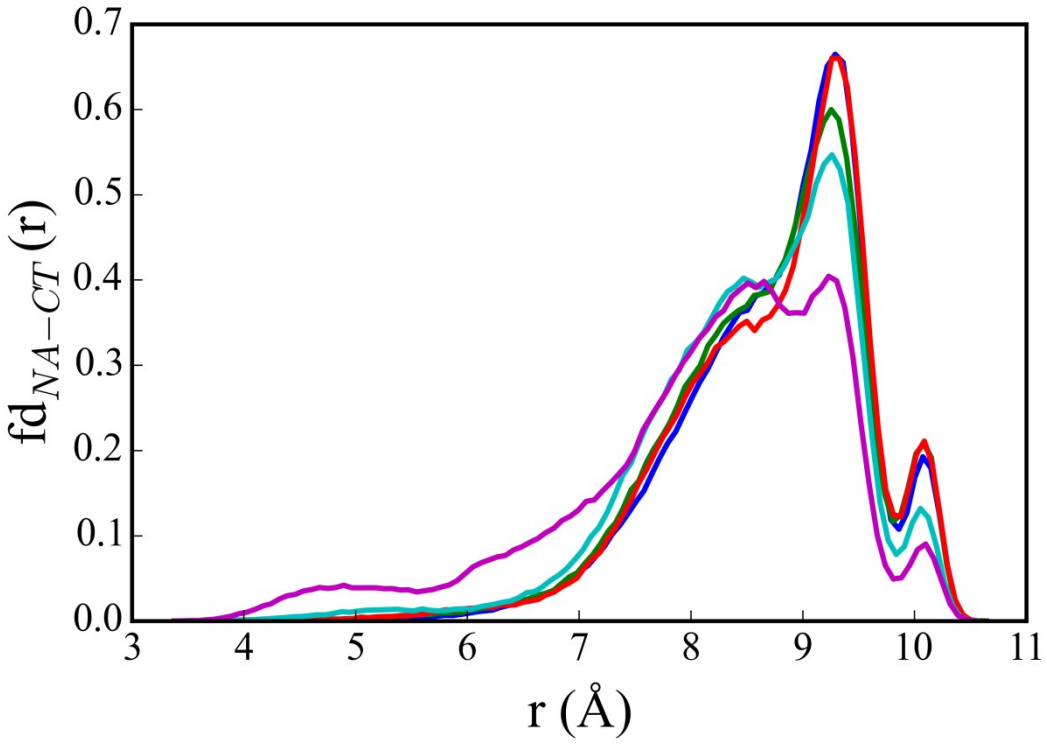

Figure S5. Length distribution, fd, for the distance between imidazolium nitrogen, NA, and terminal methyl, CT, for the various pressures studied (in order of decreasing amplitude for the peak centred at 10 Å: 1, 300, 1000, 3000 and 10000 atm, respectively).