Supplementary Material (ESI) for PCCP
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Electronic Supplementary Information
for
Viscosity of the 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid from equilibrium and nonequilibrium molecular dynamics

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I. RESULTS

A. Density comparison

The densities as a function of the temperature, obtained by Kelkar and Maginn and by us, using the same force field, are compared in Fig. 1. The experimental results from refs. [1, 2] are also plotted on this figure. Both sets of theoretical results are very close. However, we obtained a better linearity for the temperature dependence. This may be due to the fact that our computation time was longer (3 ns versus 2 ns). The estimated error bars for our results are about 0.5%. We have checked that the results no longer depended on the number of cation-anion pairs in the box, when the number of pairs was of the order of 50. This verification was performed at different values of temperature (see asterisks in figure 2). Finally, the theoretical predictions are systematically 1 to 2% larger than the experimental results.

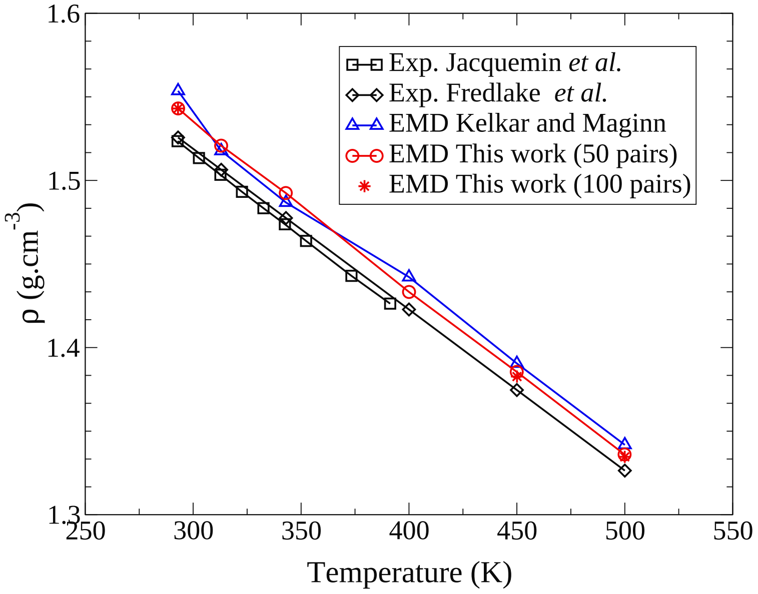


FIG. 1: (Color online) Density of [emim][Tf2N] as a function of temperature. In black: experimental data[1, 2]. In blue: Kelkar and Maginn values[3]. Red curve: our results for 50 ion pairs. Red asterisks: our results for 100 ion pairs. The size of the symbols in our results show the statistical errors.

B. Orientational relaxation time comparison

The orientational relaxation time τ_1 (first order Legendre polynomial) is calculated as the integral of the autocorrelation function of a unit vector along the molecular axis both for the anion and the cation. For this force field, the cation relaxation time corresponds to the longest orientational relaxation time of the system. The τ_1 dependence with the inverse of the temperature obtained by Kelkar and Maginn [3] and by us are presented in Fig. 2. The results are quite close on a large temperature range. The value of the relaxation time was obtained by Kelkar and Maginn by extrapolating a two stretched exponential fit of the $C_1(t)$ correlation function while we calculated this time directly by integrating the $C_1(t)$ correlation function. Our curve seems to be closer to an Arrhenius shape. Note that the relaxation time is large at room temperature (of the order of a few nanoseconds).

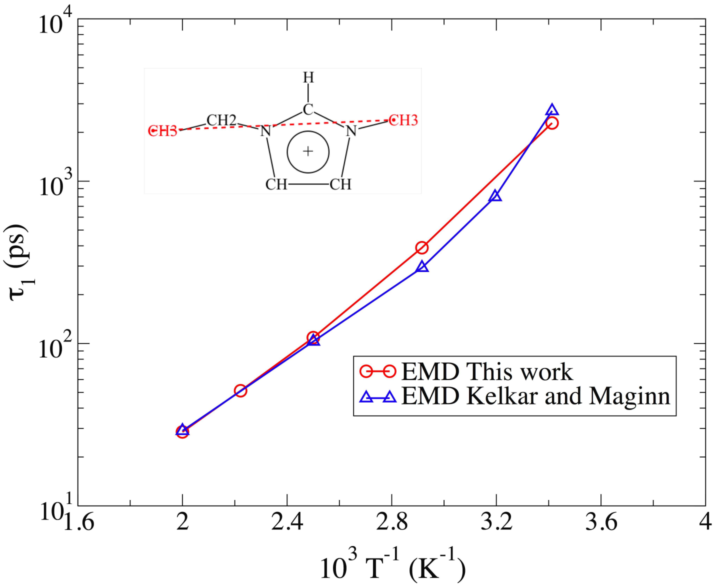


FIG. 2: (Color online) First order Legendre orientational relaxation time obtained by Kelkar and Maginn [3] (in blue) and with the Newton code (in red) *versus* inverse temperature. The unit vector is defined by the carbon positions of the methyl groups of the [emim] cation (in red on the molecule).

C. Atomic and molecular viscosities

Both the atomic and the molecular virial computations have been implemented in the Newton code. The viscosity is computed at equilibrium, using the GK formalism, from the stress tensor fluctuations. Depending on the definition chosen for the calculation of the tensor, the so-called "atomic" or "molecular" viscosities are obtained. Fig. 3 shows that both descriptions yield the same viscosity values. However, large oscillations in the atomic viscosity curve are observed for very short correlation times (lower than 1 ps, see inserted plot). This effect is due to intramolecular vibrational contributions. Similar results can be found in the literature for simpler systems [4]. To the best of our knowledge, this comparison has never been done before for complex systems such as ionic liquids. In conclusion, the calculation of the viscosity through the molecular definition using equation (2) of the article constitutes a simpler and faster algorithm compared to the traditional molecular expression and gives a more stable value.

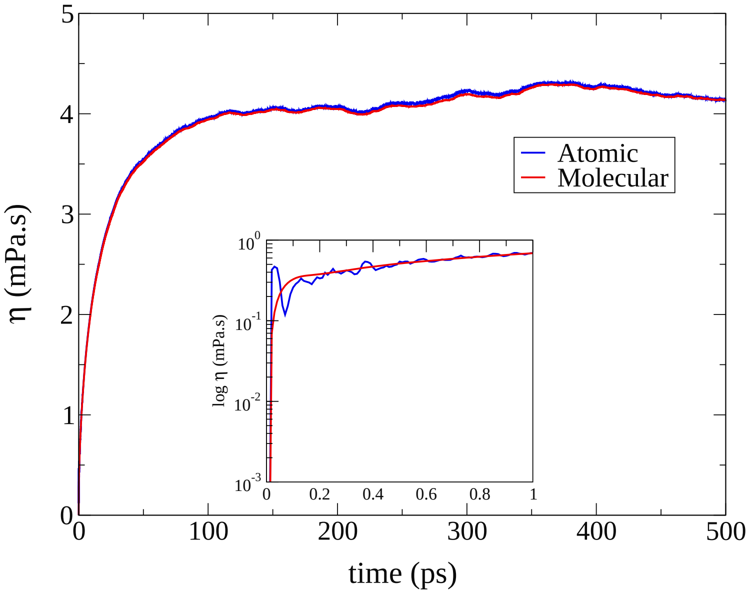


FIG. 3: (Color online) Green-Kubo viscosities *versus* time. The atomic (resp. molecular) viscosity is represented in blue (resp. in red). The atomic and molecular viscosities at very short correlation time are shown in the inserted plot. These results were obtained from a 25 ns simulation using the Newton code.

D. RNEMD velocity profile

We present below the velocity profiles (velocity in the x direction *versus* z direction) obtained using the RNEMD algorithm, for different swap period. The shear rate at a given swap period is computed from the slope, assuming a linear profil. The velocity values close to the boundaries are excluded from the linear fit.

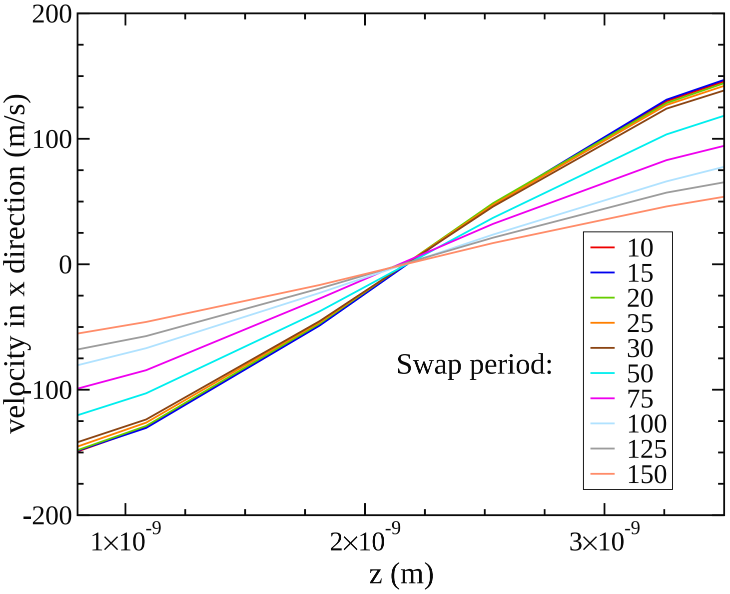
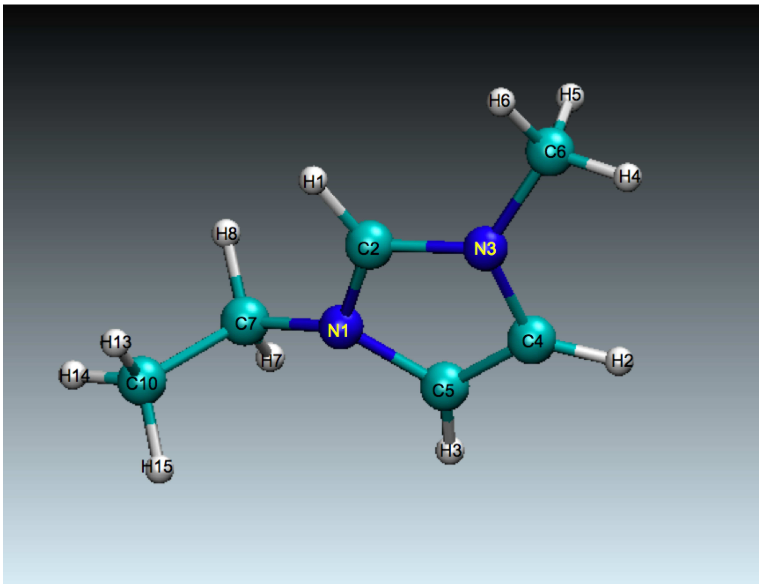


FIG. 4: (Color online) Velocity profiles obtained using the RNEMD algorithm, for different swap period.



II. [EMIM] FORCE FIELD PARAMETERS

Parameters for the [emim] cation were taken from the work of Kelkar and Maginn[3]. Partial charges were determined using the CHELPG algorithm on the electron densities calculated at B3LYP/6311-G* level (Gaussian03).

A. Dispersion-repulsion and charge potentials

$$U(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

Symbol Type	Atomic Number	m (g mol^{-1})	ϵ (kJ mol^{-1})	σ (Å)	q (e)
C5	6	12.0112	0.0500	3.207	-0.134873
C4	6	12.0112	0.0500	3.207	-0.147177
C2	6	12.0112	0.0500	3.207	-0.091215
N1	7	14.0064	0.2000	3.296	0.059417
H3	1	1.0080	0.0078	2.616	0.220374
H2	1	1.0080	0.0078	2.616	0.209995
H1	1	1.0080	0.0460	1.604	0.218877
N3	7	14.0064	0.2000	3.296	0.193715
C6	6	12.0112	0.0200	4.054	-0.250840
H4	1	1.0080	0.0220	2.352	0.145165
H5	1	1.0080	0.0220	2.352	0.145165
H6	1	1.0080	0.0220	2.352	0.145165
C7	6	12.0112	0.0200	4.054	0.103944
H7	1	1.0080	0.0220	2.352	0.055550
H8	1	1.0080	0.0220	2.352	0.055550
C10	6	12.0112	0.0550	3.875	-0.104555
H13	1	1.0080	0.0220	2.352	0.058581
H14	1	1.0080	0.0220	2.352	0.058581
H15	1	1.0080	0.0220	2.352	0.058581

B. Equivalent symbols

CPH1 = C4 C5
CPH2 = C2
NR1 = N1 N3
HR3 = H3 H2
HR1 = H1
CN7B = C6 C7
HN7 = H4 H5 H6 H7 H8 H13 H14 H15
CT2 = C8 C9
CT3 = C10

C. Bond potential

$$U(r_{ij}) = k_{\mathrm{b}}(r_{ij} - r_0)^2$$

Bond Type	r_0 (Å)	k_{b} (kcal mol^{-1} Å^{-2})
CN7B-NR1	1.4762	220.0
CPH1-NR1	1.3819	400.0
CPH2-NR1	1.3366	400.0
CPH1-CPH1	1.3610	410.0
CPH2-HR1	1.0779	340.0
CPH1-HR3	1.0775	365.0
CN7B-HN7	1.0899	309.0
CT3-HN7	1.0935	322.0
CN7B-CT3	1.5308	200.0

D. Angle potential

$$U(\theta_{ijk}) = k_a(\theta_{ijk} - \theta_0)^2$$

Angle Type	θ_0 (deg)	k_a (kcal mol^{-1} rad^{-2})
CT2-CN7B-NR1	112.34	140.00
CPH1-NR1-CPH2	108.25	130.00
HN7-CN7B-NR1	109.41	30.00
HR1-CPH2-NR1	125.44	25.00
NR1-CPH1-CPH1	107.28	130.00
NR1-CPH2-NR1	109.11	130.00
HR3-CPH1-CPH1	130.74	25.00
NR1-CPH1-HR3	122.04	25.00
HN7-CN7B-HN7	108.44	35.50
HN7-CN7B-CT2	111.68	33.40
HN7-CT2-CN7B	109.13	33.40
CN7B-CT2-CT2	111.50	58.35
CT2-CT2-CT3	112.34	58.00
HN7-CT2-HN7	106.13	35.50
HN7-CT3-HN7	107.24	35.50
CT2-CT2-HN7	108.43	26.50
CT3-CT2-HN7	109.47	34.60
CT2-CT3-HN7	111.62	34.60
CN7B-NR1-CPH2	125.75	130.00
CN7B-NR1-CPH1	125.67	130.00
CT3-CN7B-NR1	112.34	140.00
HN7-CN7B-CT3	111.68	33.40
HN7-CT3-CN7B	109.13	33.40
CT2-CT2-CT2	114.27	58.35

E. Proper dihedral angle potential

$$U(\phi_{ijkl}) = A[1 + \cos(n\phi_{ijkl} - \delta)]$$

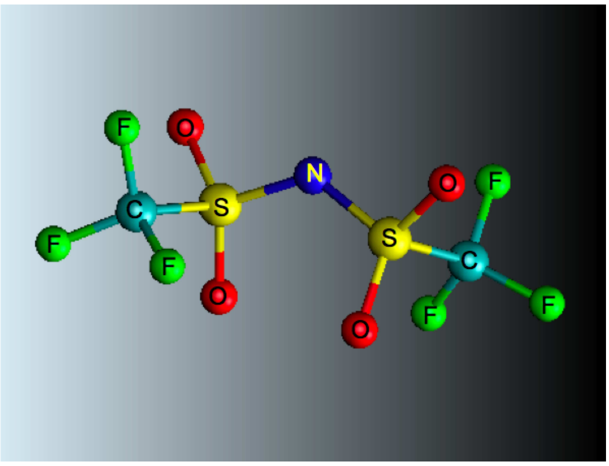
Dihedral Angle Type	A_1 (kcal mol^{-1})	δ (deg)	n
CPH2-NR1-CPH1-CPH1	14.0000	180	2
NR1-CPH1-CPH1-NR1	14.0000	180	2
NR1-CPH2-NR1-CPH1	14.0000	180	2
HR1-CPH2-NR1-CPH1	3.0000	180	2
HR3-CPH1-CPH1-HR3	2.0000	180	2
CPH1-CPH1-NR1-CN7B	0.0000	0	1
HR3-CPH1-NR1-CPH2	3.0000	180	2
NR1-CPH1-CPH1-HR3	3.0000	180	2
NR1-CPH2-NR1-CN7B	0.0000	180	2
HR1-CPH2-NR1-CN7B	0.0000	180	2
HR3-CPH1-NR1-CN7B	0.0000	180	2
CPH2-NR1-CN7B-HN7	0.1950	180	2
CPH1-NR1-CN7B-HN7	0.0000	0	3
CPH2-NR1-CN7B-CT2	0.1000	180	3
CPH1-NR1-CN7B-CT2	0.2000	0	4
NR1-CN7B-CT2-CT2	0.0000	0	3
HN7-CT2-CT3-HN7	0.1600	0	3

Proper Dihedral Angle Type	A_1 (kcal mol^{-1})	δ (deg)	n
CT2-CT2-CT3-HN7	0.1600	0	3
NR1-CN7B-CT2-HN7	0.0000	0	3
CN7B-CT2-CT2-CT3	0.1500	0	1
HN7-CN7B-CT2-HN7	0.1950	0	3
HN7-CN7B-CT2-CT2	0.1950	0	3
HN7-CT2-CT2-HN7	0.1950	0	3
CN7B-CT2-CT2-HN7	0.1950	0	3
HN7-CT2-CT2-CT3	0.1950	0	3
CPH2-NR1-CN7B-CT3	0.1000	180	3
CPH1-NR1-CN7B-CT3	0.2000	0	4
NR1-CN7B-CT3-HN7	0.0000	0	3
HN7-CN7B-CT3-HN7	0.1950	0	3
CT2-CT2-CT2-CT2	0.1950	0	3
CT2-CT2-CT2-CT3	0.1950	0	3
CN7B-CT2-CT2-CT2	0.1950	0	3
CT2-CT2-CT2-HN7	0.1950	0	3

F. Improper dihedral angle potential

$$U(\psi_{ijkl}) = A(\psi_{ijkl} - \psi_0)^2$$

Improper Dihedral Angle Type	A (kcal mol^{-1})	ψ_0 (deg)
CPH2-NR1-NR1-HR1	0.50	0.00
NR1-CPH1-CPH2-CN7B	0.60	0.00
CPH1-CPH1-NR1-HR3	0.50	0.00



III. [TF2N] FORCE FIELD PARAMETERS

Force field parameters for the [Tf2N] anion were determined by Lopes and Padua [5]. However, we have used the more recent values published on their website. Partial charges were determined using the CHELPG algorithm on the electron densities calculated at MP2/cc-pVTZ(-f) level (Gaussian98 A.9) with some extra criteria for the transferability along a homologous series and along a functional group.

A. Dispersion-repulsion and charge potentials

$$U(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

Symbol Type	Atomic Number	m (g mol^{-1})	ϵ (kJ mol^{-1})	σ (Å)	q (e)
C	6	12.0107	0.27614	3.50	+0.35
F	9	18.9984	0.22175	2.95	-0.16
S	16	32.0650	1.04600	3.55	+1.02
O	8	15.9994	0.87864	2.96	-0.53
N	7	14.0067	0.71128	3.25	-0.66

B. Bond potential

$U(r_{ij}) = \frac{k_b}{2}(r_{ij} - r_0)^2$

Bond Type	r_0 (Å)	k_b (kJ mol^{-1} Å^{-2})
C-F	1.323	3698.0
C-S	1.818	1950.0
S-O	1.442	5331.0
N-S	1.570	3137.0

C. Angle potential

$U(\theta_{ijk}) = \frac{k_a}{2}(\theta_{ijk} - \theta_0)^2$

Angle Type	θ_0 (deg)	k_a (kJ mol^{-1} rad^{-2})
F-C-F	107.1	781
S-C-F	111.8	694
C-S-O	102.6	870
O-S-O	118.5	969
O-S-N	113.6	789
C-S-N	100.2	764
S-N-S	125.6	671

D. Proper dihedral angle potential

$U(\phi_{ijkl}) = \frac{1}{2}\left(A_1(1 + \cos(\phi_{ijkl})) + A_2(1 - \cos(2\phi_{ijkl})) + A_3(1 + \cos(3\phi_{ijkl}))\right)$

Proper Dihedral Angle Type	A_1 (kJ mol^{-1})	A_2 (kJ mol^{-1})	A_3 (kJ mol^{-1})
F-C-S-O	0.0	0.000	1.451
S-N-S-O	0.0	0.000	-0.015
F-C-S-N	0.0	0.000	1.322
S-N-S-C	32.773	-10.420	-3.195

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