Supplementary material to

"The intermolecular NOE is strongly influenced by dynamics"

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University of Vienna, Department of Computational Biological Chemistry, Währinger Straße 17, 1090 Vienna, Austria (Dated: February 12, 2015) Here we present the coarse-grained (CG) model of the ionic liquid EMIM⁺ OTf⁻ developed and used within the context of our work. This includes a presentation of all model parameters and a comparison of structure and orientation in terms of the expansion coefficients of the angular pair correlation function to data from all-atom (AA) simulations. The AA model consists of the parameters which form the basis of our CG model. For a more detailed explanation of the development of the CG model, please refer to the Methods section of this paper.

Table S1 shows masses, Lennard Jones (LJ) parameters and partial charges of the CG model of EMIM⁺ OTf⁻. All bonds were kept rigid using the SHAKE algorithm. Bond lengths and quantities for angles and (improper) dihedral angles of EMIM⁺ can be found in Ref. 1 (the angle between H7,H6, and N1 is specified in a follow-up paper²). The bond length between the two CG sites of OTf⁻ is 1.861 Å.

	$m \; [\mathrm{amu}]$	σ [Å]	$\varepsilon \; [\rm kcal \; mol^{-1}]$	q [e]
EMIM ⁺				
N1	14.0070	4.0947	0.1696	-0.267
H2	13.0191	4.8894	0.1058	+0.504
N3	14.0070	4.0947	0.1696	-0.267
H4	13.0191	4.8894	0.1058	+0.199
H5	13.0191	4.8894	0.1058	+0.199
H6	14.0271	4.9209	0.1178	+0.240
H7	15.0351	4.9209	0.1749	+0.076
H8	15.0351	4.7570	0.2066	+0.316
OTf ⁻				
T1	75.6931	5.5001	0.0530	+0.108
Τ2	73.3702	5.9490	0.2500	-1.108

TABLE S1: Parameters of the CG model of EMIM⁺ OTf⁻: masses m in amu, LJ site radii σ in Å, LJ well-depths ε in kcal mol⁻¹, and partial charges q in e.

Our system was parametrized and simulated at 300 K. At this temperature the density was parametrized to 1.39 g/ml. The self-diffusion coefficient for EMIM⁺ is $7.7 \cdot 10^{-7}$ cm²s⁻¹, while for OTf⁻ it is $2.1 \cdot 10^{-7}$ cm²s⁻¹.

Structure and orientation were parametrized in terms of expansion coefficients of the angular pair correlation function

$$g(r, \Omega_1, \Omega_2, \Omega_{12}) = \sum_{l_1} \sum_{l_2} \sum_{l_{12}} g^{l_1, l_2, l_{12}}(r) \Phi^{l_1, l_2, l_{12}}(\Omega_1, \Omega_2, \Omega_{12}).$$
(1)

Here, Ω_1 and Ω_2 describe the orientation of molecules 1 and 2, respectively, while Ω_{12} stands for the polar angles of the vector \vec{r} joining molecular centers. The packing of molecular centers of mass is described by $g^{000}(r)$, and the higher g-coefficients with $(l_i \neq 0)$ measure the mutual orientation of molecular dipole moments or of the center of mass vector \vec{r} with one of the dipolar axes. In Fig. S1 we present pair correlation functions for $l_i = 0, 1$ $(g^{000}(r), g^{110}(r), g^{011}(r), g^{011}(r))$, showing cation-anion, cation-cation and anion-anion correlations of CG and AA models. For all these properties a consistent accordance between CG and AA models is observed. In other words, packing and mutual orientation of molecules is reproduced by our CG model fairly well.



FIG. S1. Pair correlation functions of EMIM⁺ OTf⁻ models. The newly developed CG model (blue) is compared to the underlying AA model (red).

- ¹ J. N. Canongia Lopes, J. Deschamps, and A. A. H. Pádua, J. Phys. Chem. B **108**, 2038 (2004).
- $^2\,$ J. N. Canongia Lopes, J. Deschamps, and A. A. H. Pádua, J. Phys. Chem. B $108,\,11250$ (2004).