Supporting information to:

# Molecular-scale insights into the mechanisms of ionic liquids interactions with carbon nanotubes

Andrey I. Frolov, Kathleen Kirchner, Tom Kirchner and Maxim V. Fedorov\*

Max Planck Institute for Mathematics in the Sciences, D 04103 Leipzig, Germany

# **Table of Content**

Part 1	List of abbreviations.				
Part 2	Simulation details.				
Part 3	Radial distribution functions of species in 2M EMIm-TFSI in AN solution.				
Part 4	Molecular ion orientation at the CNT surface. Definitions.				
	2D orientation maps of molecular ions at the CNT surface.				
Part 5	2D orientation maps of molecular ions at the CNT surface.				
Part 5 Part 6	2D orientation maps of molecular ions at the CNT surface. Number of molecular ions oriented parallel and perpendicular to the CNT surface.				

CNT	Carbon nanotube
TFSI	bis(trifluoromethylsulfonyl)imide anion
EMIm	1-ethyl-3-methylimidazolium cation
BMIm	1-butyl-3-methylimidazolium cation
OMIm	1-octyl-3-methylimidazolium cation
AN	acetonitrile
IL	ionic liquid
MD	molecular dynamics
RDP	radial density profile

#### Part 1. List of abbreviations.

#### Part 2. Simulation details.

#### 1) Systems under investigation.

We performed Molecular Dynamics (MD) simulations using the Gromacs 4.5 MD software package.<sup>1</sup> We simulated a segment of carbon nanotube solvated in 2M EMIm-TFSI in acetonitrile (AN) solution, neat EMIm-TFSI ionic liquid, 2M BMIm-TFSI in AN solution and 2M OMIm-TFSI in AN solution for three different surface charge densities of CNT:  $\sigma$ =-0.5, 0.0, +0.5 [e/nm<sup>2</sup>]. Additionally we performed simulations of the solutions without CNT.

#### 2) Molecular topology and force field potential parameters used in the simulations.

Firstly, we generated a molecular simulation topology for a CNT segment consisting of 384 carbon atoms (chirality (6,6), the tubule radius is 0.41 nm, the length is 3.94 nm). We used the on-line TubeGen 3.4 tool<sup>2</sup> to generate coordinates of the CNT. The CNT was oriented along the Z axis in the simulation boxes (see below). We used rectangular periodic boundary conditions, where the CNT was treated as a "periodic molecule". The positions of the CNT atoms were restrained to the initial values by harmonic potential with 1000 kJ mol<sup>-1</sup> nm<sup>-2</sup> force constant in each direction.

The Gromacs topology input file for the CNT was generated by the *x2top* program that is a part of the Gromacs 4.5 suite. We used the short-range Lennard-Jones nonbonded interaction parameters for the CNT carbon atoms which correspond to the benzene OPLS-AA (all-atom optimized molecular potential for liquid simulation)<sup>3</sup> carbon atom (opls\_145 in the Gromacs notation). The partial charges of the CNT carbons were set to -0.013020833, 0.000000000 and 0.013020833 [e] for the carbon nanotubes with  $\sigma$ =-0.5, 0.0, +0.5 [e/nm<sup>2</sup>]. (0.5 [e/nm<sup>2</sup>] corresponds to 3.1 [ $\mu$ C/cm<sup>2</sup>]). The equilibrium values for the structural parameters of the bonded interactions (bond lengths, angles) were taken from the initially generated structure of CNT, while the force constants for the bond and angle harmonic potentials were adopted from the OPLS-AA force field.<sup>3</sup> We do not use the dihedral potential for description of the system, however, the absence of dihedral potentials is compensated by the restraining potential. The non-bonded interactions in the systems were pair-wise additive. As it is common for the OPLS-AA family of force-fields, the Lennard-Jones coefficients for atoms of different kinds were obtained as a geometric mean value of the parameters of two corresponding particles:

where *i* and *j* indicate type of particle.

The OPLS-AA potential parameters were assigned to molecular ions and acetonitrile molecule with the use of Shrödinger Maestro software.<sup>4</sup> The parameters were then transformed into the Gromacs topology format. Then, we assigned to molecular ions the partial charges and dihedral angles potential parameters developed by Lopes et al.<sup>5,6</sup>.

#### 3) MD algorithms details.

We used the leap-frog integrator with 0.002 ps integration time step. For the Lennard-Jones potential we used 1.00 nm cut-off radius with shifting potential method. The neighbor list for the nonbonded interactions was updated each  $10^{\text{th}}$  integration step. For accurate evaluation of the long range Coulomb interactions we used the Particle Mesh Ewald method<sup>7</sup> with 1.10 nm cut-off radius for the real space sum and 0.12 nm spacing for the mesh in real space. The cubic B-splines were used to map the charges on the mesh.

The length of all the bonds with hydrogen atoms were fixed to the force field equilibrium values by the LINCS algorithm.<sup>8</sup>

For the NVT-ensemble (canonical ensemble) simulations we used the Berendsen thermostat<sup>9</sup> with the reference temperature of 343.15K and the relaxation time of 2.0 ps. For the NPT ensemble (isothermo-isobaric ensemble) simulations we used the Berendsen thermostat and also the Berendsen barostat.<sup>9</sup> In this case the system was coupled to an external pressure of 0.1013 MPa with the relaxation time of 1.0 ps. For the systems containing CNT, we employed a semi-isotropic barostat which can change the size of the simulation boxes only in directions perpendicular to the periodic CNT molecule. For the bulk solvent systems we used the isotropic barostat.

#### 4) Systems preparation and collection of statistics.

We generated the initial configurations of the systems with the Packmol program.<sup>10</sup> The configurations were then optimized by Gromacs using the energy minimization routine. To equilibrate the density the systems were simulated during at least 0.3 ns and up to 1.2 ns in the NPT ensemble. The simulation boxes contained 200 ion pairs (and additional molecular ions for neutralization of the CNT surface charge, if applicable) for the systems of CNT dissolved in 2M IL solution in AN. The number of AN molecules were adjusted in such a way that the volume of the simulation box after the equilibration in NPT-ensemble differed not more than 3% from system to system. The resulting volumes of the systems were in the range: 6.21- $6.23 \times 6.21$ - $6.23 \times 3.94$  nm<sup>3</sup>. The three systems containing CNT in neat EMIm-TFSI ionic liquid after equilibration in NPT ensemble had volumes in the range 6.16- $6.26 \times 6.15$ - $6.26 \times 3.94$  nm<sup>3</sup> and contained 340 ion pairs. We annealed the final configurations during 2 ns simulation time in NVT-ensemble with gradual decrease of temperature from 1000-1500K to 343.15K. We collected the statistics over subsequent 30 ns of the simulation time in NVT ensemble at 343.15K. We stored the coordinates of the systems each 0.3 ps for further analysis.

The configurations for the pure solution systems (without CNT) were generated with the Packmol program.<sup>10</sup> The number of ion pairs in 2M ionic liquid solutions in AN was 140. Number of AN molecules were 420, 336 and 175 for 2M EMIm-TFSI in AN, 2M BMIm-

TFSI in AN and 2M OMIm-TFSI in AN solutions, respectively. In the neat EMIm-TFSI system we had 238 ion pairs. The densities of the systems were equilibrated during at least 0.3 ns in NPT-ensemble. Then, the systems were simulated during 100 ns of simulation time in NVT-ensemble.

#### 5) Details of the trajectory analysis.

We calculated the RDPs and radial distribution functions of all the species with the help of  $g_rdf$  program which is a part of the Gromacs 4.5 suite. The orientation distributions were calculated with the  $g_sorient$  program of Gromacs 4.5 suite, which was modified to be able to handle cylindrical symmetry of CNTs and to be able to resolve the orientation probability density as a function of distance.

# Part 3. Radial distribution functions of species in 2M EMIm-TFSI in AN solution.



Figure S1: Radial distribution functions of species in 2M EMIm-TFSI in AN bulk solution. Center of mass – center of mass distributions.



Part 4. Molecular ion orientation at the CNT surface. Definitions.

Figure S2: Orientation of molecular ions around CNT.  $\Phi$  is the angle between "molecular vector" and a vector connecting the CNT axis and center of mass of the molecular ion (this vector is perpendicular to CNT axis). A) EMIm orientation around CNT. We define the molecular vector to be the vector connecting the alpha carbon atom of the longer alkyl chain to the carbon atom of the methyl group at the imidazolium ring. The same criteria are applied to other molecular cations: BMIm and OMIm. B) TFSI orientation around CNT. We define the molecular vector to be the vector connecting two sulphur atoms. Due to the symmetry of the TFSI ions the direction of the vector is chosen arbitrary.



Figure S3: Radial Density Profile of EMIm (top) and orientation  $(\cos(\Phi))$  probability density of EMIm as functions of distance (bottom) for 2M EMIm-TFSI in AN at  $\sigma$ =0.0 [e/nm<sup>2</sup>]. Gray arrows indicate the correspondence of peaks on the RDPs to the peaks on the orientation probability density map. Random distribution of molecular orientations would have the probability density of 0.5 for all values of  $\cos(\Phi)$  from -1 to1 (the integral of the probability

density at certain r is unity). The 2D map (bottom) shows for each r the probability density to find a molecular ion at certain orientation around CNT (more specifically, at certain value of  $\cos(\Phi)$ , see Figure S2). The value of the RDP at certain r shows the probability to find a molecule in a volume element at the distance relative to the random distribution. Thus, mapping the peaks on the RDP and the peaks on the 2D map of the ion orientation we can understand ions in which orientation make a major contribution to the corresponding peak on the RDP. As one can see, there are two peaks on the EMIm RDP (top graph) for r < 1.13 nm. The first peak (at r = 0.8 nm,  $cos(\Phi)$  of about 0) on the 2D orientation map (marked by dashed black circle) shows that the first peak on RDP is formed by EMIm ions which are parallel to the CNT surface (lay on the surface). The peaks at r = 1.0 nm,  $\cos(\Phi)$  of about 1 and -1 (marked by dashed black circles) indicate that the second peak on RDP is formed by EMIm ions which are perpendicular to the CNT surface. Here and after we use the following criteria: if  $-0.5 < \cos(\Phi) < 0.5$  (60° <  $\Phi < 120^{\circ}$ ) then we assume that molecular ion is parallel to the CNT surface, otherwise the ion is perpendicular to the CNT surface (the criteria are marked by white dashed lines on the 2D orientation map). In the case of random orientation distribution such criteria would give equal probabilities to find a molecule in parallel and perpendicular orientations to the CNT surface. Zero probability densities for all values of  $\cos(\Phi)$  at small r indicate that no molecules were observed at these distances during the whole simulation time.



### Part 5. 2D orientation maps of molecular ions at the CNT surface.



Figure S4: Cation Radial Density Profiles (first rows) and orientation probability densities as the functions of distance (second rows) for all the studied systems: A) 2M EMIm-TFSI in AN solution, B) 2M BMIm-TFSI in AN solution, C) 2M OMIm-TFSI in AN solution, D) neat EMIm-TFSI ionic liquid. Gray arrows indicate the correspondence of peaks on the RDPs to the peaks on the orientation distributions. The signs  $\parallel$  or  $\perp$  indicate that the peaks on a RDP (at which they are placed) are formed by molecular ions oriented parallel or perpendicular to the CNT surface, respectively.





Figure S5: TFSI Anion Radial Density Profiles (first rows) and orientation probability densities as the functions of distance (second rows) for all the studied systems: A) 2M EMIm-TFSI in AN solution, B) 2M BMIm-TFSI in AN solution, C) 2M OMIm-TFSI in AN solution, D) neat EMIm-TFSI ionic liquid. Gray arrows indicate the correspondence of peaks on the RDPs to the peaks on the orientation distributions. The signs  $\parallel$  or  $\perp$  indicate that the peaks on a RDP (at which they are placed) are formed by molecular ions oriented parallel or perpendicular to the CNT surface, respectively.

# Part 6. Number of molecular ions oriented parallel and perpendicular to the CNT surface.

We estimated the numbers of molecular ions oriented parallel and perpendicular to the CNT surface in the CNT solvation shell per 1 nm of the CNT length. We defined the boundary for the CNT solvation shell to be the position of the first deep minimum on the EMIm center of mass RDP in 2M EMIm-TFSI in AN solution at  $\sigma$ =0.0 [e/nm<sup>2</sup>]. The boundary is r = 1.13 nm. We calculated the average number of particles at a certain distance r around CNT in the following way:

$$n_{\Delta r=0.01nm}(r) = \rho^0 \cdot \frac{\rho(r)}{\rho^0} \cdot 2\pi r \cdot \Delta r$$

where  $\rho^0$  is the bulk density of the corresponding particles,  $\frac{\rho(r)}{\rho^0}$  is the RDP of the

corresponding particles,  $n_{\Delta r=0.01nm}(r)$  is the average number of particles at a certain distance r in the cylindrical volume segment with the difference between radii of smaller and larger cylinders of  $\Delta r$  (in our case  $\Delta r = 0.01$  nm). Here we imply the length of the CNT segment to be 1 nm.

From 2D orientation maps for each distance *r* we estimated the probability to find a particle in a parallel to the surface orientation (by integrating the  $\cos(\Phi)$  probability density at this *r* over the interval  $-0.5 < \cos(\Phi) < 0.5$ ) and the probability to find a particle in a perpendicular to the surface orientation (by integrating the  $\cos(\Phi)$  probability density at this *r* over the intervals  $0.5 < \cos(\Phi) < 1.0$  and  $-1.0 < \cos(\Phi) < -0.5$ ). The discretization of the functions on the *r* coordinate was the same as for the RDPs:  $\Delta r = 0.01$  nm.

Then we multiplied the number of particles at certain distance r by the probabilities to find a molecule at the same r in a parallel to the surface orientation and in a perpendicular to the surface orientation. We integrated the obtained functions over the interval 0 < r < 1.13 nm to estimate the number of particles oriented parallel and perpendicular to the CNT surface in the CNT solvation shell per 1 nm of the CNT length. We illustrate the resulting values on the Figure S6.



Figure S6: Number of molecular cations (first row) and anions (second row) oriented parallel ( $\parallel$ , filled bars) and oriented perpendicular ( $\perp$ , empty bars) to the CNT surface in the first solvation shell of CNT (0 < r < 1.13 nm) for different surface charge densities in all the studied systems (columns 1-4). The numbers are given per 1 nm of the CNT length.

Table S1: Ratio of the number of molecular cations (anions) oriented parallel and the number of molecular cations (anions) oriented perpendicular to the CNT surface in the solvation shell of CNT for different surface charge densities in all the studied systems. To analyze the table we define a threshold: if the number of ions in one orientation is larger more than 25% than the number of ions in another orientation then we assume that the former orientation is preferable, otherwise both of them are equally probable. Thus, if the ratio is more than 1.250 then the particles are preferably oriented *parallel* to the CNT surface, if the ratio is less than 1/1.250=0.800 then the particles are preferably oriented *perpendicular* to the CNT surface, if the ratio is more than 0.800 and less than 1.250 then both orientations are equally probable. We present the results on the Figure 5 of the main text. The table reveals the following conclusions. 1) An increase of the non-polar tail length increases propensity of imidazoliumbased cations to lay parallel to the surface. 2) At the cathode TFSI anions and cations are oriented mainly parallel to the surface. 3) At the anode the TFSI anions are oriented preferentially parallel to the surface, however the preferred orientations of cations depend on the length of non-polar tails. EMIm cations are preferentially oriented perpendicular to the surface, BMIm are in both parallel and perpendicular orientations, OMIm are preferentially oriented parallel to the surface. 4) An addition of acetonitrile into EMIm-TFSI ionic liquid does not *qualitatively* change the preferred orientations of molecular ions.

Molecular ion	System	σ=-0.5 [e/nm <sup>2</sup> ]	σ=0.0 [e/nm <sup>2</sup> ]	σ=0.5 [e/nm <sup>2</sup> ]
Cations	EMIm-TFSI (neat)	2.287	1.214	0.652
	EMIm-TFSI (2M)	2.703	1.219	0.694
	BMIm-TFSI (2M)	3.289	1.457	0.940
	OMIm-TFSI (2M)	4.352	2.202	1.676

TFSI anions	EMIm-TFSI (neat)	1.252	1.135	1.388
	EMIm-TFSI (2M)	1.303	1.081	1.604
	BMIm-TFSI (2M)	1.336	1.130	1.570
	OMIm-TFSI (2M)	1.383	1.085	1.807

## Part 7. Comparison of the radial density profiles for 2M EMIm-TFSI solution and neat EMIm-TFSI liquid normalized by the same bulk density (the density of 2M EMIm-TFSI solution).



Figure S7: First row: radial density profiles of EMIm, TFSI and AN around CNT in 2M AN EMIm-TFSI solution for the three surface charge densities on CNT:  $\sigma = -0.5$ , 0.0, +0.5 [e/nm<sup>2</sup>]. There is an asymmetry of molecular ions response to the potential created by charged CNT. Second row: radial density profiles of EMIm, TFSI around CNT in neat EMIm-TFSI solution for the three surface charge densities on CNT normalized to the bulk density of 2M EMIm-TFSI solution to facilitate comparison on the relative number of particles.

## **References:**

- 1. Hess, B., Kutzner, C., van der Spoel, D. & Lindahl, E. GROMACS 4: Algorithms for Highly Efficient, Load-Balanced, and Scalable Molecular Simulation. *Journal of Chemical Theory and Computation* **4**, 435-447 (2008).
- 2. Frey, J.T. & Doren, D.J. TubeGen Online v3.4 (web-interface), University of Delaware, Newark DE, 2011. at <a href="http://turin.nss.udel.edu/research/tubegenonline.html">http://turin.nss.udel.edu/research/tubegenonline.html</a>>
- 3. Jorgensen, W.L. & Severance, D.L. Aromatic-aromatic interactions: free energy profiles for the benzene dimer in water, chloroform, and liquid benzene. *Journal of the American Chemical Society* **112**, 4768-4774 (1990).
- 4. Schrödinger Maestro. at <http://www.schrodinger.com/>
- 5. Canongia Lopes, J.N., Deschamps, J. & Pádua, A.A.H. Modeling ionic liquids using a systematic all-atom force field. *Journal of Physical Chemistry B* **108**, 2038–2047 (2004).
- 6. Canongia Lopes, J.N. & Pádua, A.A.H. Molecular force field for ionic liquids composed of triflate or bistriflylimide anions. *Journal of Physical Chemistry B* **108**, 16893–16898 (2004).
- 7. Essmann, U. et al. A Smooth Particle Mesh Ewald Method. *Journal of Chemical Physics* **103**, 8577–8593 (1995).
- 8. Hess, B., Bekker, H., Berendsen, H. & Fraaije, J. LINCS: A linear constraint solver for molecular simulations. *Journal of Computational Chemistry* **18**, 1463-1472 (1997).
- 9. Berendsen, H., Postma, J., van Gunsteren, W., DiNola, A. & Haak, J. Molecular dynamics with coupling to an external bath. *The Journal of Chemical Physics* **81**, 3684-3690 (1984).
- Martínez, L., Andrade, R., Birgin, E.G. & Martínez, J.M. PACKMOL: a package for building initial configurations for molecular dynamics simulations. *J Comput Chem* 30, 2157-2164 (2009).