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Mixtures of LiTFSI and urea: ideal thermodynamic behavior as key to the formation of deep eutectic solvents?

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Radial distribution function for Li^+-Li^+

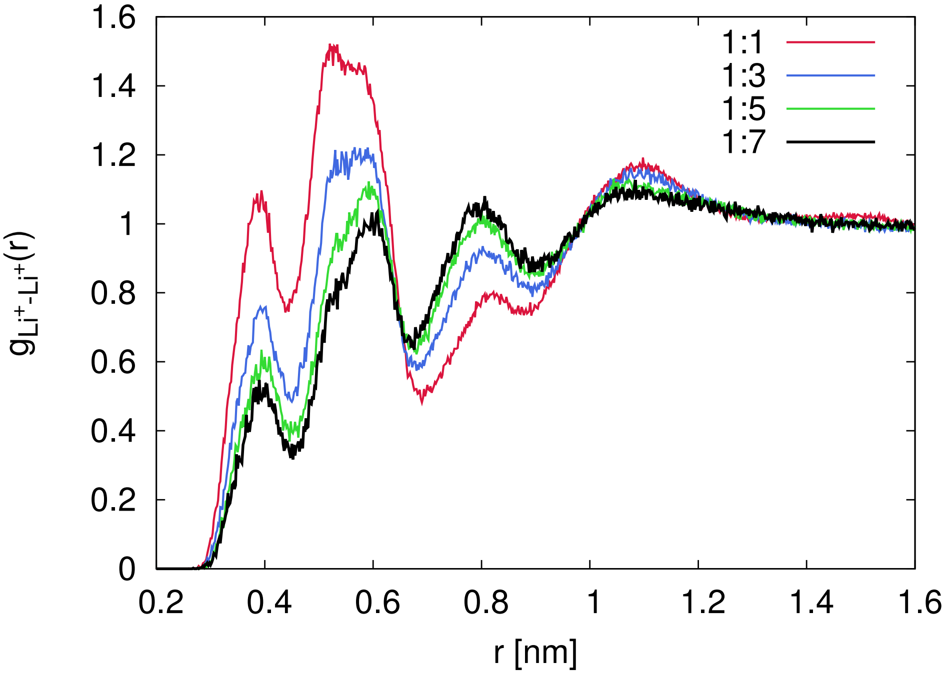

Figure 1: Radial distribution function $g_{\mathrm{Li}^+-\mathrm{Li}^+}(r)$ for Li^+ ions in various LiTFSI/urea mixtures as denoted in the legend.

Molecular snapshots: DFT calculations

$\mathbf{Li^+ \cdot [TFSI^-]_3[Urea]_1}$

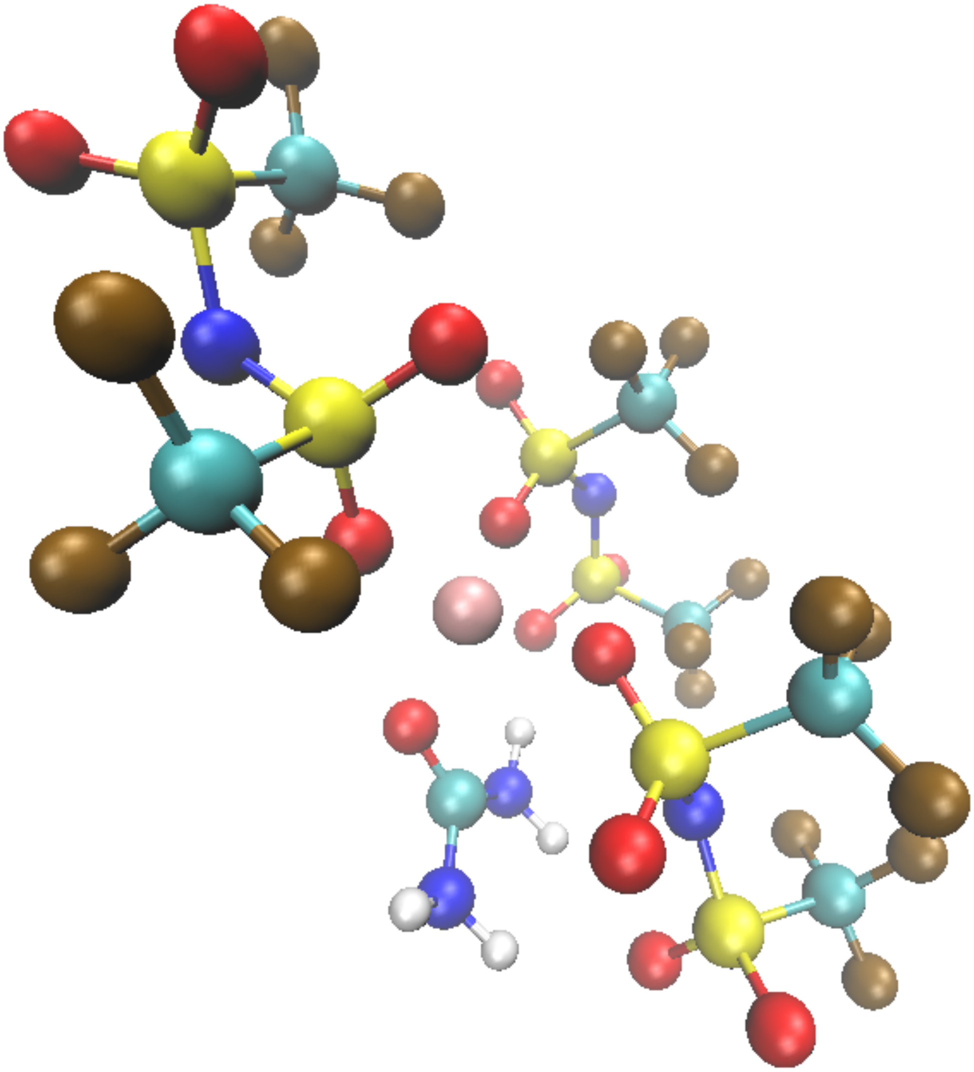

Figure 2: Molecular snapshot of a $Li^+ \cdot [TFSI^-]_3[Urea]_1$ complex from DFT calculations. Li^+ ions are colored in pink, sulfur atoms in yellow, oxygen atoms in red, fluorine atoms in brown, carbon atoms in turquoise and all hydrogen atoms are colored in white.

$Li^+ \cdot [TFSI^-]_1[Urea]_3$

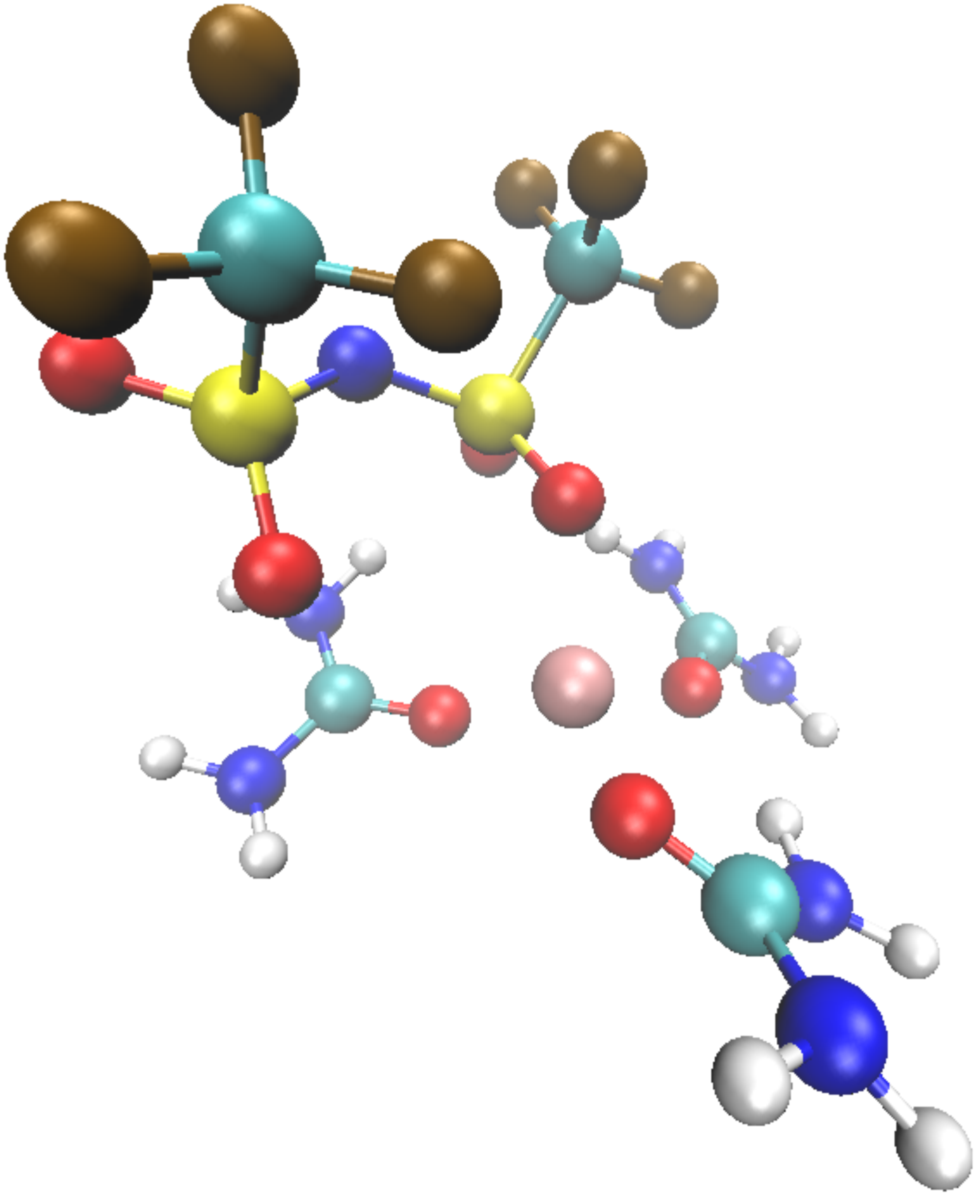

Figure 3: Molecular snapshot of a $Li^+ \cdot [TFSI^-]_1[Urea]_3$ complex from DFT calculations. Li^+ ions are colored in pink, sulfur atoms in yellow, oxygen atoms in red, fluorine atoms in brown, carbon atoms in turquoise and all hydrogen atoms are colored in white.

Dielectric constants

The relative permittivity ϵ_r, also called dielectric constant, is calculated straightforwardly by using the dipole moment fluctuation formula[1–3]

$$\epsilon_\mathrm{r} = 1 + \frac{4\pi}{3} \frac{\langle \boldsymbol{M}_\mathrm{tot}^2 \rangle}{\langle V \rangle k_\mathrm{B} T} \tag{1}$$

with Boltzmann constant k_B, and temperature T, where $\langle \boldsymbol{M}_\mathrm{tot}^2 \rangle$ denotes the average squared net total molecular dipole moment in a simulation box of average volume $\langle V \rangle$.

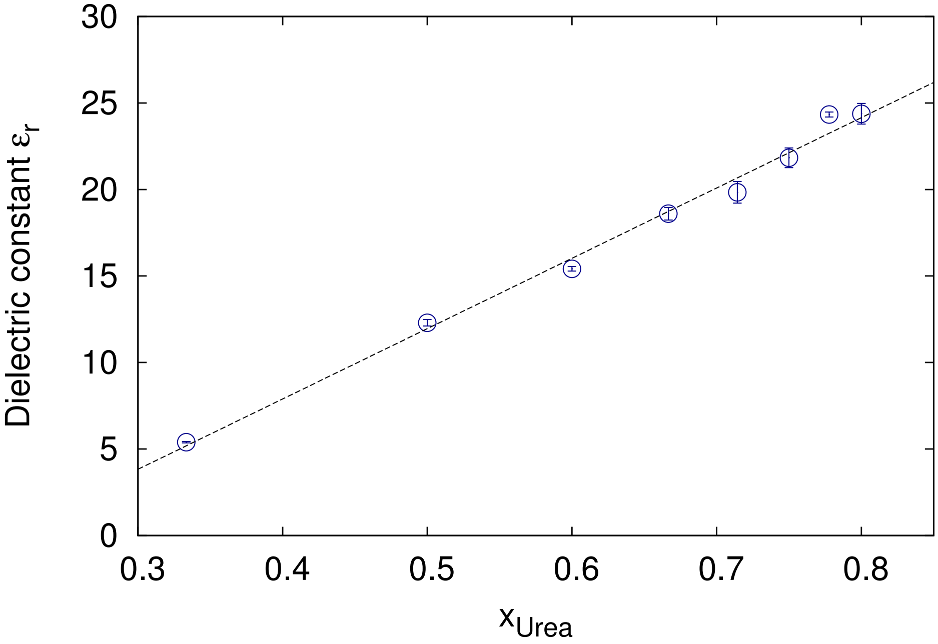

Figure 4: Dielectric constant ϵ_r of the LiTFSI/urea mixtures for different urea mole fractions x_Urea. The dashed black line shows a linear fit function via regression analysis.

Total interaction energies

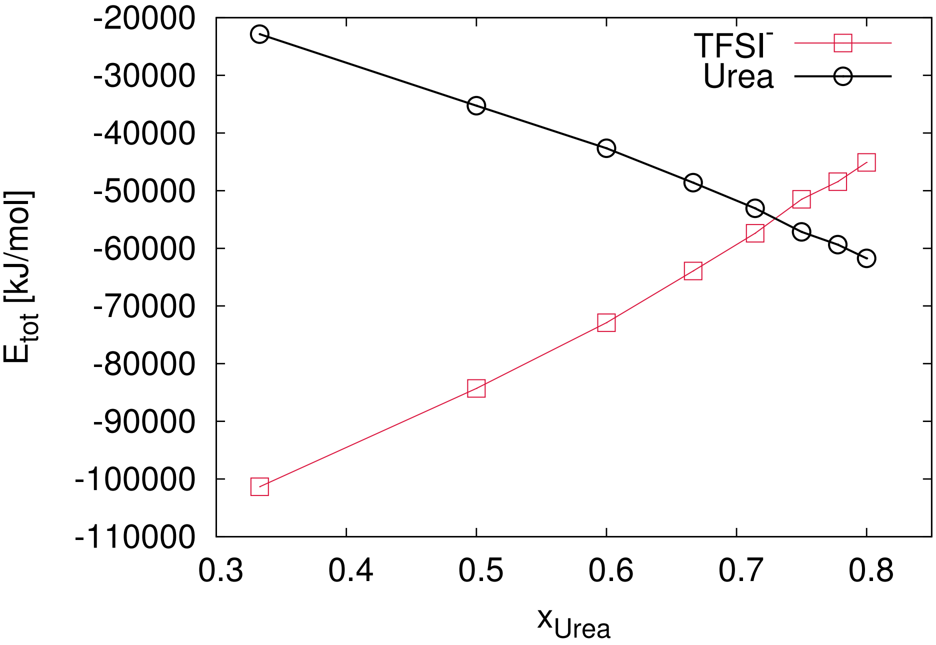

Figure 5: Total interaction energies between Li^+ and urea as well as between Li^+ and $TFSI^-$ ions, respectively. Values for Li^+–urea are shown as black circles whereas all values for Li^+–$TFSI^-$ are depicted as red squares.

Mean-squared displacement (MSD) of components

With increasing urea concentration, the MSD values increase significantly. The transition from sub-diffusive ($\sim t^{\alpha}$ with $\alpha < 1$) to diffusive regimes ($\sim t$) occurs on shorter time scales with increasing urea concentration[4]. With regard to this point, the first coordination shell around Li^{+} ions is located on length scales $r_c = 0.544$ nm. It can be assumed that diffusive behavior is observed on time scales $\tau > r_c^2/6D_{cm}$ and on length scales $\Delta r^2 > \Delta r_c^2$ as marked by the horizontal black line in Fig. 6 (top).

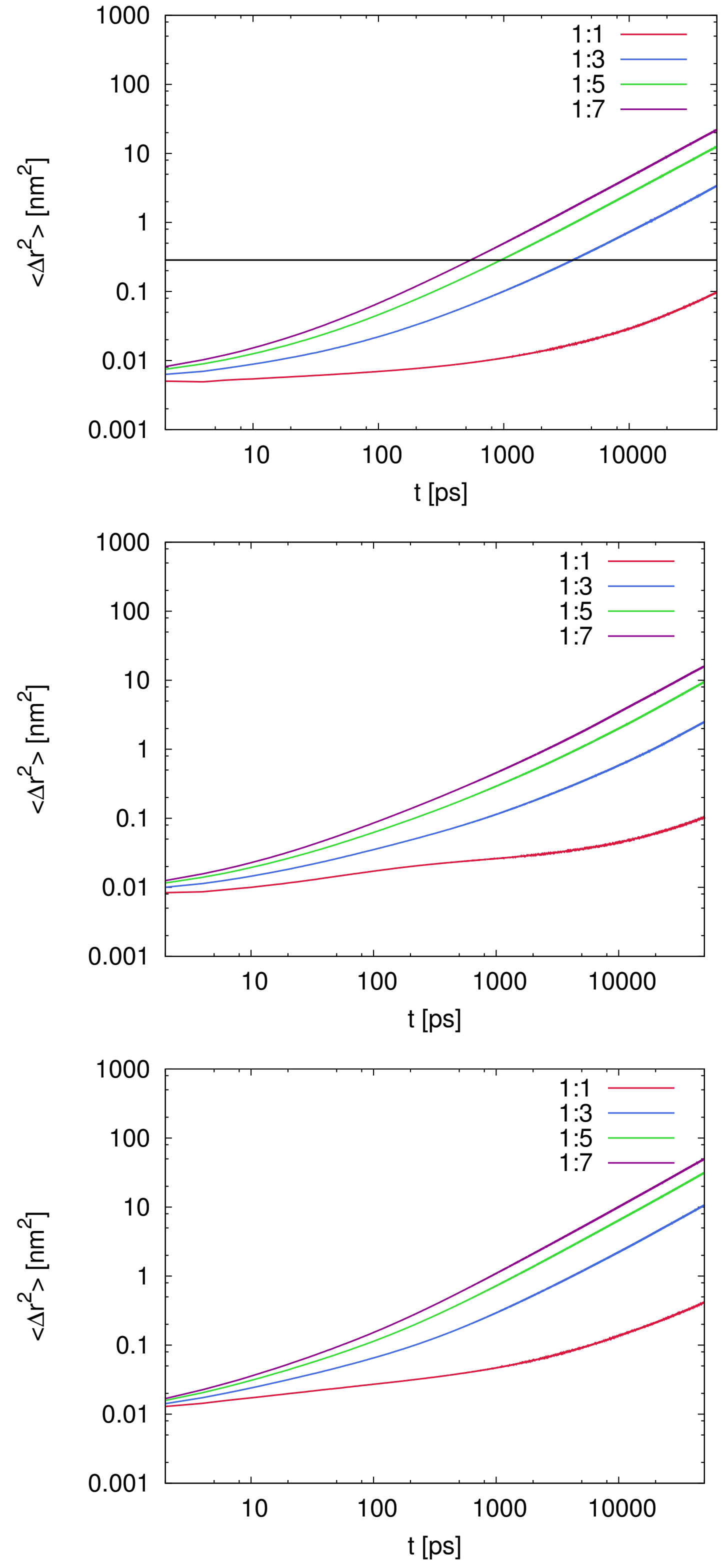

Figure 6: Mean-square displacement of Li$^+$ (top), TFSI$^-$ ions (middle) and urea molecules (bottom) for various mixing ratios as denoted in the legend.

References

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