Molecular dynamics simulation of high-frequency sound modes in ionic liquids.

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Introduction

In the spatial scale from $k \sim 0.1$ Å^{-1} up to the main peak of the static structure factor, $S(k)$, the corresponding intermolecular dynamics of viscous liquids comprises the THz frequency range. The most powerful experimental technique to probe this wave vector and frequency range, (k,ω), is inelastic X-ray scattering (IXS). Molecular dynamics simulations, MD, show that intermolecular dynamics of liquids in the wave vector range up to *ca.* half of the main peak of $S(k)$ can be projected onto plane waves giving well-defined spectra with k-dependent frequency. Fujii *et al.*[1] reported in 2013 the first investigation by IXS of ionic liquids based on the 1-ethyl-3-methylimidazolium cation, $[C_2C_1im]^+$ and the anions bis(fluorosulfonyl)imide, $[FSI]^-$, and bis(trifluoromethanesulfonyl)imide, $[TFSI]^-$, and 0.5 mol.kg^{-1} Li^+ solutions of either LiFSI or LiTFSI in each of these ionic liquids. The aim of this work is to calculate the high-frequency sound modes by MD simulations (using a classical non-polarizable force field)[2] for the same systems studied by Fujii *et al.*.[1] The MD simulations allow for the calculation of properties not promptly available from experiments, for instance, besides spectra of longitudinal acoustic modes (LA), the spectra of transverse modes (TA).

Results and Discussion

Time correlation functions of mass current were calculated for longitudinal and transverse acoustic modes, $C_{LA}(k,t)$ and $C_{TA}(k,t)$, whose Fourier transform give the corresponding spectra, $C_{LA}(k,\omega)$ and $C_{TA}(k,\omega)$. The frequency of the peak of $C_{LA}(k,\omega)$ and $C_{TA}(k,\omega)$ spectra calculated for different wave vectors give the energy excitation of LA and TA modes, *i.e.* the dispersion curve $\omega(k)$.[3]

Figure 1 compares experimental IXS data and MD results of $\omega_{LA}(k)$ and $\omega_{TA}(k)$ for the pure IL $[C_2C_1im][TFSI]$. The overall agreement between experimental and simulated dispersion curves of LA modes is good for small wave vectors, which is the relevant range as $\omega_{LA}(k)$ is linear and $C_{LA}(k,\omega)$ spectra are sharp. The inset of Figure 1 shows the wavevector dependent sound velocity, $c(k) = \omega/k$. The $c_{LA}(k)$ calculated for this system is in good agreement with experiment, in particular if one takes into account that we calculated $C_{LA}(k,\omega)$ rather than the dynamic structure factor, $S(k,\omega)$. The $c_{LA}(k)$ curve calculated for $[C_2C_1im][FSI]$ reproduces the experimental finding that excitation frequencies in this system are slightly higher than $[C_2C_1im][TFSI]$. The MD simulations showed that the high-frequency sound velocity is not sensitive to dissolution of lithium in these ionic liquids.

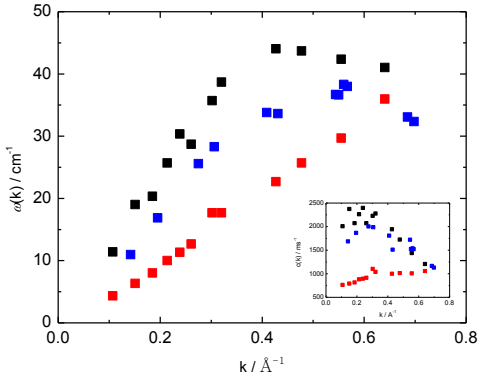

Figure 1: Dispersion curves of high-frequency sound modes of $[C_2C_1im][TFSI]$ calculated by MD simulations (LA, black; TA, red) and experiment[1] (blue). Inset: the wavevector dependent sound velocity, $c(k) = \omega/k$.

Conclusions

From the short-time high-frequency collective dynamics investigated in this work, it seems that the simulated systems are relatively stiffer than the real systems. Nevertheless, the dispersion curves recently obtained by an IXS spectroscopy study[1] of $[C_2C_1im][TFSI]$ and $[C_2C_1im][FSI]$ have been reproduced by MD simulations with non-polarizable models for ionic liquids.

Acknowledgments

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