Dynamical heterogeneity in the ionic liquid [$BMIM^+$][PF_6^-] confined in a graphitic slit pore

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Ionic liquids (ILs) have attracted extensive attention in recent years due to the potential application as electrolytes in electrochemical double-layer capacitors (EDLCs) and other electrochemical devices. Compared with traditional solutions of electrolytes, ILs offer many advantages, such as good chemical and thermal stability, negligible vapor pressure, nonflammability, high ionic conductivity, and wide electrochemical window. The dynamics of the confined ions is one important factor that determines the internal resistance in an EDLC, which ultimately affects its specific power (i.e., how quickly an EDLC can deliver energy).

In this work we have used molecular simulation to investigate the relaxation dynamics of the IL [$BMIM^+$][PF_6^-] under confinement in a slit-like graphitic pore in the temperature range of 300-450K. The dynamics of the confined IL are analyzed in detail by measuring mean squared displacements (MSDs) in different directions, van Hove correlation functions and intermediate scattering functions. The latest are then fitted to modified Kohlrausch-Williams-Watts (KWW) functions to attempt to quantify the timescales associated with the α and β relaxation processes. All these properties, when combined with measurements of different structural properties (local density profiles, radial distribution functions, etc.), can be used to detect and characterize spatial heterogeneities in the dynamics of the IL. Our results suggest that the local relaxation dynamics of the ions depend strongly on their position inside the pore. Close to the pore walls, the typical relaxation times are larger than those for the ions in the center of the pore. Cations have faster relaxation times than anions everywhere in the system. Important spatial heterogeneities in the dynamics of the confined IL are observed, and those are compared against results observed for the same IL in bulk systems at the same temperatures.