Stochastic Structure Determination for Conformationally Flexible Clusters: CrazyLego

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Ionic liquids (ILs) are a subset of molten salts distinguished by having melting points below 100°C. The physical, rheological and electrical properties of ILs may be potentially tuned through judicious choice of anion and cation structure. Of myriad possible ILs, only a small fraction will possess the desired properties to make them useful in any given application. Thus, a method towards systematically understanding IL structure and properties, that does not rely on (expensive) chemical synthesis, is required.

We present the CrazyLego method, a stochastic structure generator, that unlike previous implementations of the “Kick" algorithm[1], is fully conformer-aware. The conformer, rotation and position of each fragment are all chosen stochastically. Structures are then optimized using dispersion-corrected 3rd order SCC-DFTB (DFTB3).[2]

Using CrazyLego, we have determined the structures and properties of imidazolium-nitrate IL clusters, $([\mathrm{xMIM}]^+[\mathrm{NO_3}]^-)_n$ for x=D,E,B and alkylammonium-nitrate clusters, $([\mathrm{xAN}]^+[\mathrm{NO_3}]^-)_n$ for x=E,P,B for up to n=10 ion pairs. We compute binding energies, Radial Distribution Functions (RDFs) and hydrogen bonding properties of each IL cluster and show the emergence of bulk properties at surprisingly modest cluster sizes of only 7-10 ion pairs.

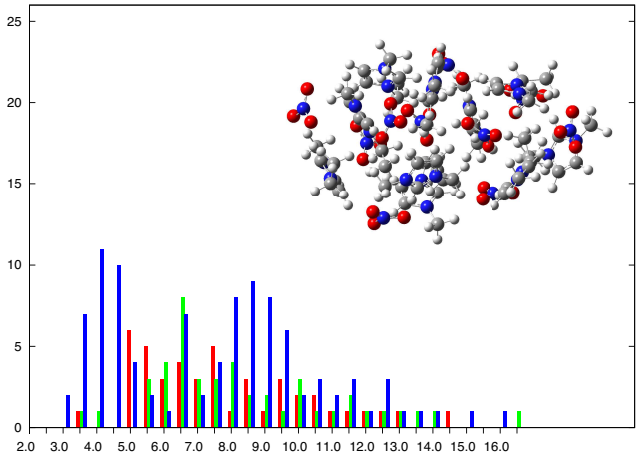

Figure 1: Cation-anion (blue), anion-anion (green) and cation-cation (red) distance distributions for inter-centroid distances of $([\mathrm{EMIM}]^+[\mathrm{NO_3}]^-)_{10}$.

[1] Addicoat, M. A., Metha, G. F. *J. Comput. Chem.*, 30:57-64, 2009.

[2] Gaus, M., Cui, Q., Elstner, M., *J. Chem. Theory. Comput.*, 7:931-948, 2011.