Critical analysis of liquid structure models

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The structure of liquids is studied with molecular dynamics (MD) using density functional theory (DFT). The radial distribution function (RDF) may be directly computed from the simulations, which represents the probability of finding an atom at a given distance from a reference atom [1]. Fluctuations in the RDF thus correspond to shells of systematic lower and higher density. Liquid structure is experimentally usually examined by measuring the structure factor (SF) in neutron diffraction experiments, which relates to the RDF in real space through a Fourier transform. By varying isotopes in the molecules, the total/partial and intermolecular/intramolecular RDFs may be fitted [2].

However, when not all isotope variations are carried out, there remains uncertainty in the extraction of the RDFs from the total experimental SFs. Our contribution shows that experimental RDFs [3], indirectly derived from measured SFs, may show spectacularly large discrepancies with the computed RDFs [4]. We have investigated the molecular liquids like methanol, ethanol, chloroform, acetonitrile, and tetrahydrofuran. Our MD simulations are capable of providing structural information for those cases where not all isotope variations have been performed in diffraction experiments.

Moreover, a correction scheme is set up for the Basis Set Superposition Error (BSSE), which results from using an incomplete localized basis set for expanding the atomic and molecular orbitals, causing an artificial strengthening of the intermolecular interactions and artificial shortening of intermolecular distances [5]. The new proposed correction models is a classical force field energy term, whose parameters are fitted to data obtained from a first MD run, and which can be added with low computational cost to subsequent MD runs [4,6]. Also dispersion is taken into account. Our results with the correction model show that the RDF peaks are affected, either lowered or increased. A systematic correction can not be predicted as the effect depends on the overall density. Validation with several other density functionals and liquids is currently being prepared.

References:

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