Functional Equation of State for Species with Non-Central Dipole: Co-Oriented Fluid Functional Equation for Electrostatic Interactions

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The description and prediction of thermo-physical properties has undergone substantial progress in the past decades especially using equations of state (EOS). Still, there are many substances, which cannot be described with this kind of theory. This is especially true, if not only pure compounds, but also mixtures are considered. Substances that have a polar character and tend to form local structures have turned out to be especially challenging to model. Probably the best known substance from this class is water.

In this contribution, we focus on much simpler molecules, namely three model fluids:

a) The well-known Stockmayer fluid with a Lennard-Jones (LJ) sphere and a central dipole.

b) A model with a LJ sphere and a dipole shifted from the center along its axis.

Despite their simplicity, no EOS is currently available that can model all these substances without additional parameter fitting.

We present here a new perturbation approach that allows incorporating the unknown structure of the dipolar models in the form of their orientation distribution function (ODF) without the need for iterations. The missing parameters of the resulting functional equation of state – Co-Oriented Fluid Functional Equation for Electrostatic interactions (COFFEE) – are fit to our molecular simulation data of model a)'s vapor-liquid equilibrium (VLE) and ODF. Its predictions for the VLE and ODF of model b) with different dipole moments and shifts of the dipole are compared to our molecular simulations of the same properties. Although being first order in the unknown orientation distribution only, the EOS accurately predicts VLE at low and intermediate dipole moments. COFFEE is applied to the description of hydrogen chloride and shows substantial improvement compared to other state-of-the-art theories.