Molecular Thermodynamics Approach to the Relative Permittivity

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The relative permittivity of a fluid is an important property that is also indicative of its thermodynamic behavior. For example, a high relative permittivity is characteristic for a polar fluid which can dissolve salts. However, for many industrially relevant fluids, experimental data for the relative permittivity are scarce. Thus, a predictive modeling approach for the relative permittivity is desirable. In the present work, first steps in this direction are taken using molecular dynamics (MD) simulations and the recently developed molecular thermodynamics framework COFFEE [1] (Co-Oriented Fluid Functional Equation for Electrostatic Interactions).

First, the relative permittivity of molecular models for 25 industrially relevant fluids is predicted by sampling Kirkwood's formula [2] in MD simulations. To this end, molecular models for a wide variety of fluids, ranging from slightly to strongly polar, are taken from the literature. Most of the studied models underestimate the relative permittivity; however, the models which describe the relative permittivity accurately typically do so for wide ranges of temperature and pressure [3].

Then, a predictive approach towards the relative permittivity of Stockmayer-type model fluids is developed based on COFFEE. The predictions obtained from COFFEE are assessed by comparison to a comprehensive set of MD simulation data, covering the entire fluid region, i.e. gaseous, liquid and supercritical states. Reasonable agreement between COFFEE and the MD data is observed. By closer examination of the MD data, a universal scaling behavior of the relative permittivity as a function of temperature and density is revealed [4,5].

References

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