Statistical Thermodynamics (Simulation & Equation of state)

Thermophysical properties prediction: towards a unified approach

Samy Khennache[1], Hai Hoang[2], Stéphanie Delage Santacreu[3], Romain Privat[4], Guillaume Galliéro[1]
[1]Universite de Pau et des Pays de l'Adour, E2S UPPA, CNRS, TOTAL, LFCR, UMR5150, Pau, France.
[2]Institute of Fundamental and Applied Sciences, Duy Tan University, Tran Nhat Duat Street, District 1, Ho Chi Minh City 700000, Vietnam.
[3]Universite de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPRA, LMAP, UMR5142, Pau, France
[4]Université de Lorraine, École Nationale Supérieure des Industries Chimiques, LRGP (UMR CNRS 7274), 54000, Nancy, France.

samy.khennache@univ-pau.fr

Developing a generic force field, that, when combined with molecular simulations, allows to predict both transport and equilibrium properties of fluids in various thermodynamics conditions is still a challenge [1-3]. Fine Grained (FG) force fields are the most popular ones, but their parameterizations are not an easy task and are often done on equilibrium properties only. As an alternative Coarse Grained (CG) force fields possess several interesting features relatively to FG models. First, they are simpler to parameterize. Second, they require a smaller amount of CPU time. Third, if appropriately chosen, they can be combined with theories to directly predict their properties avoiding then the need of molecular simulations.

Among the available CG force fields, the one based on the Lennard-Jones (LJ) chain, that consists in LJ particles freely and tangentially bonded, is known to describe well the equilibrium properties with only three parameters per non polar species, as exemplified by the success of some SAFT equations of state. However, this molecular model is not able to yield accurate transport properties, such as viscosity, of molecular fluids [1]. To alleviate this weakness a forth molecular parameter can be added as done when the LJ potential is replaced by Mie potential [2, 4]. This Mie CG force field provides very good results for small molecular compounds [4], but exhibit a systematic underestimation of the liquid viscosity [5], explained by the fully flexible nature of the molecules represented by such CG force field.

Thus, in this work, we propose a new CG force field that integrates a variable rigidity in a LJ chain model as the additional forth parameter, named hereafter the RLJC force field. To determine the four molecular parameters, we have employed a top-down parameterization strategy thanks to the principle of corresponding states, similarly to what proposed in refs [2] and [4]. It will be shown during the presentation that this simple CG force field is able to provide good thermodynamic and transport properties of various compounds for a wide range of thermodynamics conditions.

References:

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