

***Ab Initio* Potentials for Predicting Thermodynamic Properties and Fluid Phase Equilibria**

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Historically, the prediction of thermodynamic properties and fluid phase equilibria [1] has relied on approximate theoretical models. In particular, equations of state [2] have provided a computationally attractive calculation method and considerable progress has been achieved in the development of sophisticated models that include a high level of molecular detail [3]. The accuracy of prediction has improved greatly, particularly for macromolecules. However, from a theoretical perspective, molecular simulation [4] is the method of choice for predictions because it can be applied with relatively few theoretical assumptions. A comparison of molecular simulation data with experiment also serves to unambiguously validate the underlying theoretical model. In a conventional molecular simulation study, the choice of intermolecular potential is the main theoretical assumption. We note that this too can be avoided by using ‘on the fly’ methods, such as Car-Parrinello [5] molecular dynamics. The practice of molecular simulation has, in part, mirrored early equation of state calculations in so far as the choice of intermolecular potential is often based on empirical considerations. The sophisticated force fields [4] that accurately determine the properties of macromolecules and proteins are composed of empirical components. For example, most include the Lennard-Jones potential or a similar empirical term for the non-bonded interactions. In contrast, advances in computational chemistry mean that accurate potentials are being developed [6] from first principles. The ‘state-of-the-art’ in *ab initio* potentials is largely confined to two-body interactions. This is a problem for both thermodynamic properties and phase equilibria, which are noticeably affected by multi-body interactions. In this work, we examine the accuracy of *ab initio* potentials to calculate both vapor-liquid equilibria and thermodynamic properties such as heat capacities, thermal expansion coefficient, speed of sound etc. [7]. The investigation ranges from noble gas atoms to some encouraging results for molecules, such as water. The method produces insights into the underlying interactions that are responsible for the observed macroscopic properties. We demonstrate how multi-body effects such as three-body interactions and polarization can be added to *ab initio* potentials to considerably improve their predictive accuracy. This means that *ab initio* potentials can be used as the theoretical backbone for the systematic improvement of the prediction of thermodynamic properties and phase equilibria.

References:

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