Ab Initio Prediction of the Thermophysical Properties and Vapor-Liquid Equilibria of Hydrogen

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There is plenty of incentive to accurately predict the properties of molecular hydrogen because of its increasingly important role in the global economy [1]. The quantum nature of hydrogen often means that theoretically rigorous first principles determination of its intermolecular interactions requires solving the Schrödinger equation with a post-Hartree–Fock method. The focus of previous attempts [2-4] to develop an intermolecular potential for hydrogen has been to determine its cryogenic behavior that is genuinely affected by quantum behavior. However, quantum interactions are not an important consideration for applications that occur at relatively high temperatures, which means that incorporating them is sometimes counter-productive to accurate predictions. In particular, the critical properties of hydrogen that are commonly used as inputs to both theory and equation of state modelling [5] are arguably inappropriate beyond cryogenic conditions.

We have recently reported [6] a classical intermolecular potential that combines *ab initio* data for two-body interactions with a three-body potential that addresses this issue. The potential yields classical values of the critical properties, resulting in accurate predictions of the second virial coefficients and pressure-volume-temperature behavior. This work uses molecular simulation [7] to determine the thermophysical properties and vapor-liquid equilibria of both pure hydrogen and some of its key hydrogen mixtures. The significance of the classical potential is that it improves the *a priori* prediction of mixtures by reducing the reliance on combining rules for unlike mixture properties.

References

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