Thermodynamic Properties from Combining Intermolecular Potentials

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The macroscopic properties and behavior of materials are ultimately determined by the nature of interaction between the constituent atoms or molecules. These interactions can be rigorously evaluated via molecular simulation using a suitable intermolecular potential, which means the accuracy of the intermolecular potential is the key aspect of obtaining accurate predictions. Historically, using the simple procedure of summing the individual contributions to interatomic and/or intermolecular interactions has generated useful intermolecular potentials for fluids. This approach has been used for empirical potentials, sophisticated force fields and ab initio potentials obtained from first principles. A considerable amount of information is captured in the development of intermolecular potentials, which often cannot be re-used for new situation.

In this work, we examine how knowledge gained from existing potentials can be utilised for new situation with minimal loss of information. A procedure for combining intermolecular potentials is proposed. The usefulness of the resulting combined potentials are investigated by reporting molecular simulations for both vapor-liquid-equilibria and thermodynamic properties. The supercritical behavior is investigated for thermodynamic properties such as the isochoric heat capacity, thermal pressure coefficient and thermal expansion coefficient, and the Joule-Thomson coefficient. Significantly, the combined potentials procedure can be used to represent the effects of both two-body only and two-body plus three-body interactions. This is achieved without the usual complexity of ab initio potentials for these types of interactions.