

Thermodynamic perturbation theory for fused sphere hard chain fluids using nonadditive interactions

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A model is developed for the equation of state of fused chains based on Wertheim thermodynamic perturbation theory and nonadditive size interactions. The model also assumes that the structure (represented by the radial distribution function) of the fused chain fluid is the same as that of the touching hard sphere chain fluid. The model is completely based on spherical additive and nonadditive size interactions. The model has the advantage of offering good agreement with simulation data while at the same time being independent of fitted parameters. The model is most accurate for short chains, small values of Δ (slightly fused spheres) and at intermediate (liquidlike) densities. © 2004 American Institute of Physics. [DOI: 10.1063/1.1647527]

INTRODUCTION

Many of the equilibrium properties of fluids can be satisfactorily treated within the frame work of models that take into account repulsive interactions only. As a result, real molecules have been modeled as hard convex bodies, the simplest of which are hard spheres. Similar to small molecules which can be represented by single hard spheres or dumbbels, polymers can be represented by tangent hard sphere chains. These models provide good representation of two important features of the chain; excluded volume and connectivity.¹ Furthermore, the hard sphere chain model can be used as a reference system for perturbation theories of more realistic polymeric systems. Theoretical modeling of these systems is simpler and their simulation is less computationally expensive than real polymers. Several approaches have been used to derive the equation of state of tangent hard spheres. The general perturbation theories of Wertheim and their extensions (TPT1, TPT2, and TPT-dimer) are among the earliest and most accurate models of the equation of state of tangent hard spheres.²⁻⁷ Other accurate approaches are the generalized Flory (GF) theory pioneered by Hall,⁸⁻¹⁰ the extended scaled particle theory,¹¹ and Percus–Yevick integral equation theory.¹² A review of the equation of state theories of hard chains was given by Sadus.¹³

In real polymers, the bond length between adjacent atoms in the chain is smaller than the average of their diameters. Consequently, the fused hard sphere model which allows overlap between adjacent hard spheres is closer to real representation of the real chain than tangent hard sphere models. For example, the bond length to monomer diameter

ratio in polyethylene is 0.4.¹ However, the equation of state of fused hard chains is not as well developed as the tangent hard sphere equations of state. This is because there is no simple and well-defined monomer or dimer that can be used as reference fluid for the TPT or GF theories.¹

The TPT1 equation of state has been extended to represent FHS chain fluids using the scaled particle theory parameter α at the second virial coefficient level.^{11,13-15} The resulting equation of state is accurate, however, it requires knowledge of the second virial coefficient. Another TPT1 extension suggested replacing the FHS molecules with equivalent tangent hard sphere molecules.¹⁶ This method, however was limited in accuracy to small chains. Jackson and Gubbins¹⁷ and Phan *et al.*¹⁸ used interpolation schemes to extend TPT1 to FHS chains. However, accuracy of the models deteriorated substantially as chain length increased.¹⁸ The reference fluid of the TPT theory has also been modified by adjusting the reference monomer size and volume fraction in such a way to improve the performance of the equation.¹

The GF theories have also been extended to FHS chain fluids by finding appropriate reference fluids.¹ Honnel and Hall adjusted the theory by assuming that the size of the reference monomer or fused dimer are equivalent to those of the FHS chain, but the number of beads was adjusted to make their mole fractions identical to those of the FHS chain fluid.⁹ Yetheraj *et al.* used a similar approach in which the number of beads per unit volume and the bond length of the reference dimer were the same as the FHS chain fluid, but the diameters of the monomer and underlying fused dimer were adjusted in such away that the volume fraction was the same as the FHS chain fluid.¹⁹ Costa *et al.* refined the reference monomer and dimer fluids further to yield more accurate results.²⁰

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