Comparison of Hard-Sphere Chain Models with Molecular Simulation Data

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Abstract
The proposed equation of state predicts the compressibility factors of hard-sphere fluids as similar to widely used Carnahan-Starling equation of state. The new theory, the theory of Sadus and the thermodynamic perturbation dimer theory (TPT-D) of hard sphere chains have been compared with available simulation data. The percent average absolute deviations have also been calculated. From the study of this work one can bring a conclusion that the theory can be used to construct equations of state for polymers having short and long chain molecules.

Keywords: *Carnahan-Starling Equation of State; Virial Series; Compressibility Factor; Average Absolute Deviation.*

Introduction

The development of equations of state for hard-sphere chain is of fundamental importance to many industrial applications. The concept of the hard-sphere chain provides the theoretical backbone for an equation of state for chainlike molecules that has an exact role of the hard-sphere concept for simple molecules. One of the most accurate and simplest hard-sphere equations of state was derived by Carnahan and Starling (CS)(1989).The CS equation was obtained by approximating the hard-sphere virial series equation using a closed form equation. The CS hard-sphere equation is typically used to model the repulsive behavior of molecules in theoretically based equation of state. While the CS equation is accurate in the prediction of compressibility factor of hard-sphere fluids over a wide range of densities, it is not accurate in the meta-stable region. Although the hard-sphere concept is used successfully for equations of state of simple molecules, the hard-sphere chain concept is the essential part of equations of state for large molecules, e.g., polymers. Honnell and Hall (1989), Chapman et al.(1989), Chang and Sandler (1994), Sadus (1995,1996), and Cheng et al.(2004) proposed equations of state for hard-sphere chains of molecules. These equations generally agree well with molecular simulation data, however, they are relatively complex for engineering applications.

Equation of Nasrifar et al.(2006) have noticed that a ratio of second-order polynomials can reasonably describe the compressibility of hard-sphere fluids for a wide range of densities between the ideal gas density and the closed packed density. Based on these observations they derived a simple and accurate hard-sphere equation in terms of a ratio of second-order polynomials.

Theory

One may express the proposed close-packed density corrected (CDC) equation (2006) in the

following form:

$$Z_{hs} = 1 + \frac{4\eta + (6 - 4\lambda)}{(1-\eta)(1-\lambda\eta)} \qquad (1)$$

Werteim (1997) and Chapman et al. (1988) developed the thermodynamic perturbation theory(TPT) of hard-sphere chain fluids. The TPT theory may be expressed by

$$Z_m = 1 + m(Z_{hs} - 1) - (m-1)\eta \frac{\partial g_{hs}(\sigma)}{\partial \eta} \qquad (2)$$

where m denotes the number of monomer sites in a chain-like molecule and $g_{hs}(\sigma)$ is the site-site correlation function at contact for hard-spheres. The parameter for packing fraction, η is given by

$$\eta = m \frac{\pi\sigma^3}{6}\rho \qquad (3)$$

where σ is the hard-sphere diameter and ρ is the number density.

Equation (8) is simple and is in good agreement with molecular simulation data. Chang and Sandler has expressed the thermodynamic perturbation-dimer theory (TPT-D) as

$$Z_m^{Dimer} = 1 + m(Z_{hs} - 1) - \frac{m}{2}\eta \frac{\partial g_{hs}(\sigma)}{\partial \eta} - \frac{(m-2)}{2}\eta \frac{\partial g_{hd}(\sigma)}{\partial \eta} \qquad (4)$$

where $g_{hd}(\sigma)$ is the site-site correlation function at contact for hard dimers.

The thermodynamic perturbation-dimer /monomer theory (TPT-D/M) is derived by the differential equation

$$g_{hd}(\sigma) = C[g^{hs}(\sigma)]^{2^{1/3}} \qquad (5)$$

Equation (1) relates the site-site correlation function at contact for hard dimmers to the site-site correlation function at contact for hard spheres. The constant C of eqn.(1) can be determined using the low-density boundary condition, i.e., $g^{hs}(\sigma) \to 1$ and $g^{hd}(\sigma) \to 0.5$ as $\eta \to 0$. With this boundary condition the value of the constant is: $C = 0.5$. Therefore eqn.(1) takes the form:

$$g_{hd}(\sigma) = 0.5[g^{hs}(\sigma)]^{2^{1/3}} \qquad (6)$$

The calculated site-site correlations at contact for hard dimmers are calculated for Carnahan Starling (CS) and close density packed (CDC) and are compared in Figure 1 with molecular simulation data. We have also calculated the site-site correlation function at contact from the equations of Chang and Sandler (Eq. 9), Ghonasgi and Chapman (Eq. 10) and the hard sphere site-site correlation function of our work. These have been compared with the simulation data as shown in Figure 1. These are summarized as follows:

$$g_{CS}^{hs}(\sigma) = \frac{1 - \frac{\eta}{2}}{(1-\eta)^3} \qquad (7)$$

$$g_{CDC}^{hs}(\sigma) = \frac{1 + \left(\frac{3}{2} - \lambda\right)\eta}{(1-\eta)(1-\lambda\eta)} \qquad (8)$$

$$g_1^{hs}(\sigma) = \frac{(2-\eta)(0.534 + 0.414\eta)}{2(1-\eta)^3} \qquad (9)$$

$$g_2^{hs}(\sigma) = \frac{1 + 2\eta + 26.45031\eta^{6.17}}{2(1-\eta)^2} \qquad (10)$$

$$g_3^{hs}(\sigma) = \frac{f_0 + f_1 - f_0^2\eta}{4(1 - f_0\eta)^2} \qquad (11)$$

where $g_1^{hs}(\sigma)$, $g_2^{hs}(\sigma)$ and $g_3^{hs}(\sigma)$ are the site-site correlation function at contact from Chapman and Sandler (1994), Chapman et al. (1988) and Sadus (1995) respectively. In eqn.(11) $f_0 = 1.3021$ and $f_1 = 2.9045$. The average absolute deviations between simulation results and equation of state calculations are summarized in Table 1. It is apparent from the analysis that the TPT of CS and TPT of CDC are less accurate than the STPT-D.

Table I Average absolute deviation (%AAD) in predicting hard-sphere chain compressibility factors using different equations.

Mer	N	TPT (Ghonasgi and Chapman)	TPT CDC	STPT
32	11	9.22	9.78	9.02
51	12	10.05	10.44	9.13
201	11	15.01	15.00	9.77
Overall	34	11.427	11.74	9.307

$$\%AAD = (100/n)\Sigma_j^n \left| calculated_j - Simulated_j \right| / Simulated_j.$$

Conclusions

The values predicted from the hard-dimer correlation function at contact are in good agreement with the molecular simulation data. Particularly because of the accuracy, the TPT EOS can be used for real chain like fluids such as n-alkanes and polymers.
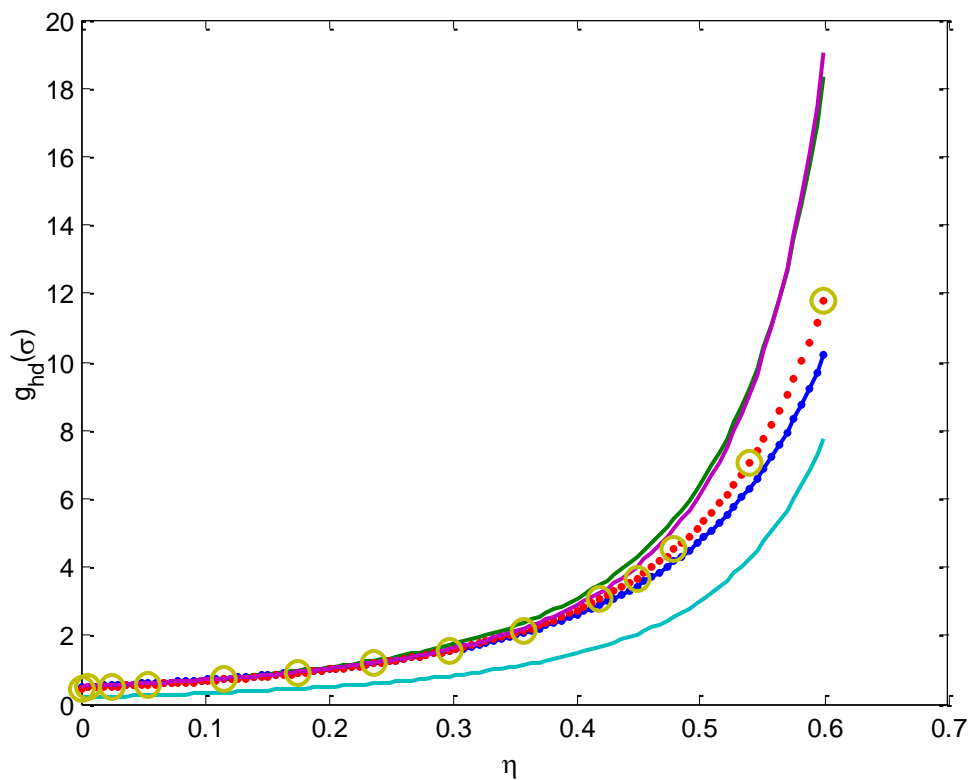
Figure 1 Simulated [4] and predicted site-site correlation functions at contact for hard dimmers.
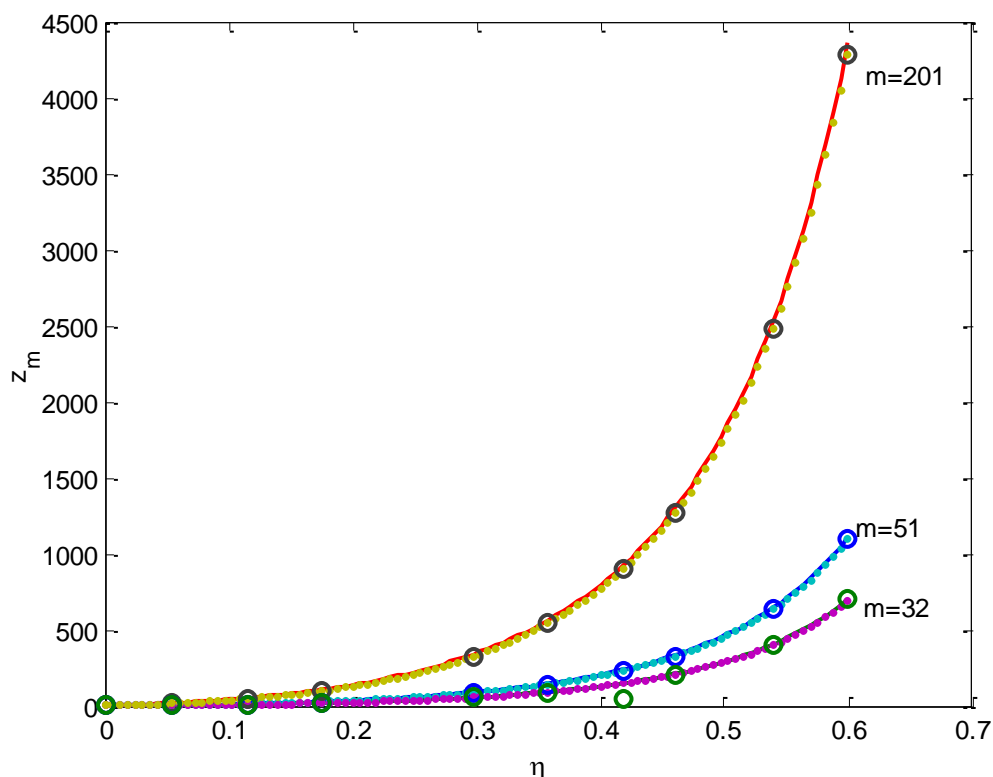
Figure 2 Simulated [4,10] and predicted hard-sphere chain compressibility factor from TPT-D (Sadus & Ghonasngi and Capman) theories combined with CDC EoS.

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