CHAPTER-4

EQUATION OF STATE OF LINEAR FUSED HARD SPHERE CHAIN FLUIDS

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4.1. **INTRODUCTION**

The tangent hard sphere chain model has attracted wide-spread attention because it takes into account two important features of polymer chain bead connectivity and excluded volume. The hard sphere chain model (or "pearl-necklace" model) provides an intuitively appealing starting point for the study of chain fluids. Each molecule is modeled as a series of freely jointed, tangent, hard spheres which interact through site-site potentials. As a result, temperature does not influence the configurational space distribution of the chains and the fluid is athermal. Use of a pearl-necklace model simplifies the nature of the site-site interactions while retaining the essential geometric features of the chain, and allows one to explore the effects of molecular geometry and internal flexibility on the local structure of the fluid. At the same time, the hard chain system can serve as a reference fluid about which attractive interactions may be introduced as perturbation. In this sense, the pearl-necklace model can play an important role in the study of more realistic chain fluids analogous to that played by the hard-sphere monomer in the study of more complex monatomic fluids.

The study of the equation of state for the homonuclear hard sphere chain fluid has received much attention in recent years. There have been several theories for predicting the equation of state of linear chain molecules such as perturbation theories [1-3], Percus-Yevick (PY) theory [4], generalized Flory-dimer theory (GFD) [5] and statistical associating fluid theory (SAFT) [6]. The advantage of SAFT theory is that it requires the equation of state of the monomer only. The SAFT equation of state has yielded good results for short chains but becomes worse for longer chain molecules. It has been improved by Ghonasgi and Chapman [7], leading to SAFT-D theory but it is limited to tangent hard sphere chain molecules. The equation of state in SAFT-D
theory requires only the contact values of the hard spheres and hard dispheres site-site correlation functions. The theory can be applied readily to the tangent molecules having longer chain lengths with certain modifications. Hence, the present work re-examines the equation of state of SAFT-D theory. The theory employed the contact value of the correlation function \( g(\sigma) \) of the dimer proposed by Chiew [8], who has derived two analytical expressions for the average correlation function at contact as a function of chain length \( m \) and hard sphere site volume \( \eta \). Ghonasgi and Chapman [7] have employed the expression for \( g(\sigma) \) of the dimer with an assumption that the correlation function at contact of the dimer, tetramer, octamer and so on will remain the same. Recently, we have proposed the equation of state of hard chain molecules using SAFT-D theory [9], by applying the expression for \( g(\sigma) \) for \( m \) components separately without making any assumption. We have found that the equations of state obtained by using chain length dependent expression of \( g(\sigma) \) predict better result than those obtained by Ghonasgi and Chapman. In this chapter, we consider the long chain molecules having 51mers and 200 mers. The numerical determinations of EOS of 50 mers and 200 mers focus the possibility of describing the EOS by the addition of equations of state of its segments. We also show in this work that the equation of state of LTHS chain can be transformed into LFHS chain by considering a suitable value of chain length \( m^* \). We have applied our model based on SAFT-D theory in predicting the volumetric behaviour of the fused hard sphere fluid consisting of different mers at different bond length \( \ell^* \). We also examine the accuracy of this approach to generalize for other models of LTHS system at same bond length \( \ell^* \). We find SAFT-D theory predicts good
values for the compressibility factor of fused hard sphere chain molecules and also a
good agreement with MC simulation results in all cases. The SAFT-D theory
describes better equation of state in comparison to GFD theory for longer chain
molecules.

4.2. STATISTICAL ASSOCIATING FLUID-DIMER THEORY FOR LINEAR
TANGENT CHAIN MOLECULES

The extension of Wertheim theory [1] resulted in an equation of state for
associating chain molecules called the statistical associating fluid theory
(SAFT). SAFT predicts poor results for EOS and second virial coefficient for
longer chain length. Ghonasgi and chapman [7] have improved the SAFT by
introducing hard dimer reference system.

Ghonasgi and chapman [7] consider a pure fluid in which the molecules
can be represented as chain formed from spheres bonded to each other. They
consider that \( N_o \) be the number of chains. Each chain has \( m \) hard spheres or
segments of equal diameter (Homonuclear) bonded to each other. Each sphere
forming the chain is numbered as component 1,2,3,4,.......\( m \). component 1 has
one association site; so component 1 can form only one bond with another
component. Component 2 has two sites, 3 has two sites, and so on. Finally
component \( m \) has one association site. The bonding between the components
is restricted such that component 1 can only bond to component 2, component
2 can only bond to components 1 and 3, and so on. Finally component \( m \) can
only bond to component \( m-1 \). When the extension of Wertheim’s theory to
mixtures is applied, the change in compressibility factor due to association can be written as\[6\],

\[
Z_{\text{assoc}} = Z_{\text{total}} - Z_{\text{ref}} = \rho_c \sum_{\beta=1}^{m} \frac{1}{\Gamma(\beta)} \left( \frac{1}{X_A^{(\beta)}} - \frac{1}{2} \right)
\]

\[Z_{\text{ref}} = \frac{P_{\text{ref}}}{\rho k T}\]
is the compressibility factor for the reference fluid, in this case hard spheres, \(\beta\) is the number of the component, \(X_A^{(\beta)}\) is the fraction of component \(\beta\) not bonded at site \(A\). \(\Gamma(\beta)\) is the set of all sites on component \(\beta\), \(\rho\) is the number density of the spheres, and \(\rho_c\) is the density of each component which is also equal to the density of chains. Since each site can bond with only one type of site \(X_A = X\) for all sites on all components. An expression for \(X\) can be derived from the theory; this expression is given by \[6\],

\[
\left( \frac{1}{X} \right)^2 - \frac{1}{X} - \rho_c \Delta = 0
\]

\(\Delta\) is defined by

\[\Delta = \int g_R(12)f(12)d(12)\]

where \(g_R(12)\) is the reference fluid pair correlation function; the reference fluid in this case is the hard sphere fluid. The symbol \(\int d(12)\) denotes an unweighted average over all orientations of molecules 1 and 2 and integration over all separations of molecules 1 and 2. The notation (12) represents the positions and orientations of molecules 1 and 2. \(f(12) = \exp(-\phi_{assoc}/ kT)\) is
the Mayer f function for the association interaction. Total bonding conditions are imposed on the mixture by making the association energy very high. At total bonding all X’s → 0 and the association bonds become “covalent bonds.” Because of the restrictions on bonding, the total bonding limit can be taken directly [1, 6].

Ghonasgi and Chapman assume that the spheres bond tangently so that the Mayer f function becomes a delta function, \( f(r) = \delta(r-\sigma) \). They have also considered molecules with variable bond length. Taking the derivative of \( X \) with respect to density from equation (4.2) and substituting into Equation (4.1) and applying the total bonding condition, Eqn.(4.1) becomes

\[
Z_{\text{chain}}^{\text{chain}} = \frac{\rho_c}{\rho} (m-1) \left\{ 1 + \rho \frac{\partial \ln g_{\text{HS}}(\sigma)}{\partial \rho} \right\}
\]  

(4.4)

Where \( \rho / \rho_c = m \), \( g_{\text{HS}}(\sigma) \) is the hard sphere radial distribution function at contact, and \( \sigma \) is the hard sphere diameter. The total compressibility factor in terms of the density of chains can be written as

\[
Z^{\text{HC}} = mZ^{\text{HS}} - (m-1) \left\{ 1 + \eta \frac{\partial \ln g_{\text{HS}}(\sigma)}{\partial \eta} \right\}
\]  

(4.5)

Where \( \eta \) is the packing fraction or the volume fraction and is defined as \( \eta = \pi \rho_c m \sigma^3 / 6 \). Equation (4.5) is the reference and chain part of the SAFT Equation of state. If we use the Carnahan-Starling [10] Equation of state for \( Z^{\text{HS}} \) and \( g_{\text{HS}}(\sigma) \) equation (4.5) becomes
\[ Z^{HC} = \frac{m}{(1-\eta)^3} \left[ \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3} - (m-1) \frac{1 + \eta - \eta^2 / 2}{(1-\eta)(1-\eta/2)} \right] \quad (4.6a) \]

Where

\[ Z^{HS} = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3} \quad (4.6b) \]

The SAFT equation of state has been shown to be in good agreement for chains with up to eight bonded spheres [1, 6]. For 16 segments the SAFT EOS slightly overpredicts the pressure. When compared to recent simulation data [11] or longer chains of up to 201 spheres SAFT predictions becomes worse, though it still shows the correct qualitative trend. It is also known that SAFT does not give a good prediction for the second virial coefficients as the chain length increases. Ghonasgi and Chapman [7] improved SAFT by adding some information about the dimer.

They consider a mixture of m components which are hard sphere, there are \( N_c \) number each component and each pair of m (assuming m is even) spheres bond to form dispheres. SAFT gives good estimate for the compressibility factor of disphere molecules [6,7]. The second virial coefficient from SAFT for dispheres is also in good agreement with the exact second virial coefficient calculated analytically [13]. The equation of state of this disphere fluid can be written from Eqs(4.5) as

\[ Z^{HD} = 2Z^{HS} - \left[ 1 + \eta \frac{\partial \ln g_{HS}(\sigma)}{\partial \eta} \right] \quad (4.7) \]
Further they bond each pair of dispheres to form chains which are four segments long, the equation of state for tetramers is given by

$$Z^{HT} = 2Z^{HD} - \left( 1 + \eta \frac{\partial \ln g_{HD}(\sigma)}{\partial \eta} \right)$$  \hspace{1cm} (4.8)

$g_{HD}(\sigma)$ is the site-site correlation function at contact for hard dispheres. Substituting Eq (4.7) into Eq (4.8) one can obtain,

$$Z^{HT} = 4Z^{HS} - 2 \left( 1 + \eta \frac{\partial \ln g_{HS}(\sigma)}{\partial \eta} \right) - \left( 1 + \eta \frac{\partial \ln g_{HD}(\sigma)}{\partial \eta} \right)$$  \hspace{1cm} (4.9)

Now bond each pair of tetramers to form chains of eight segments long (octamers) using the same procedure as described above, the equation of state of octamers can be written as

$$Z^{HO} = 8Z^{HS} - 4 \left( 1 + \eta \frac{\partial \ln g_{HS}(\sigma)}{\partial \eta} \right) - 2 \left( 1 + \eta \frac{\partial \ln g_{HD}(\sigma)}{\partial \eta} \right) - \left( 1 + \eta \frac{\partial \ln g_{HT}(\sigma)}{\partial \eta} \right)$$  \hspace{1cm} (4.10)

$g_{HT}(\sigma)$ is the site-site correlation function at contact for the terminal spheres in a chain of segments long.

In a fluid of chain molecules the value of the site-site distribution function at contact is lower than that of a fluid of spheres at the same packing fraction. This effect is called the “correlation hole” effect [14]. The correlation hole is the region surrounding each segment where segments from other chains are excluded. Due to the correlation hole effect $g_{HS}(\sigma) > g_{HD}(\sigma) > g_{HT}(\sigma)$ at the
same packing fraction. Chiew [8, 15] has obtained the intermolecular site-site correlation functions of freely jointed tangent hard sphere chains with in the context of the Percus-Yevick (PY) integral equation theory. Chiew [8] obtained the site-site correlation functions for chains of four segments long. Further Chiew[8] obtained the intermolecular pair correlation function for a general hard chain m segments long. The site-site correlation functions at contact for terminal spheres given by PY theory are identical for hard dispheres and hard tetrasheres at the same packing fractions.

In order to verify Ghonasgi and Chapman compare the values of Chiew results and simulation values of the site-site correlation function for hard dispheres and tetrasheres. They find good agreement between simulation values and Chiew results for hard dispheres from low packing fraction to a packing fraction about 0.35. Since only the density derivative of the log of the site-site correlation function is important in equation (4.10), one can assume that \( \frac{\partial \ln g_{HH}(\sigma)}{\partial \eta} = \frac{\partial \ln g_{HD}(\sigma)}{\partial \eta} \). Thus Eq.(4.10) takes the form

\[
Z^{HO} = 8Z^{HS} - 4 \left( 1 + \eta \frac{\partial \ln g_{HS}(\sigma)}{\partial \eta} \right) - 3 \left( 1 + \eta \frac{\partial \ln g_{HD}(\sigma)}{\partial \eta} \right)
\]

(4.11)

If it is assume that all the chain longer than dispheres have the same density dependence of the site-site correlation function for the terminal segments at contact that Eqs.(4.9),(4.10) and (4.11) can be generalized as

\[
Z^m = mZ^{HS} - \frac{m}{2} \left( 1 + \eta \frac{\partial \ln g_{HS}(\sigma)}{\partial \eta} \right) - \left( \frac{m}{2} - 1 \right) \left( 1 + \eta \frac{\partial \ln g_{HD}(\sigma)}{\partial \eta} \right)
\]

(4.12)
This is SAFT-Dimer (SAFT-D) equation of state. Chiew [8] results for $g_{HD}(\sigma)$ is given by

$$g_{HD}(\sigma) = \frac{1 + 2\eta}{2(1 - \eta)^2} \quad (4.13)$$

$g_{HS}(\sigma)$ from the Carnahan and Starling Equation of state is given by

$$g_{HS}(\sigma) = \frac{(2 - \eta)}{2(1 - \eta)^3} \quad (4.14)$$

After differentiating Eqs. (4.13) and (4.14) with respect to packing fraction and substituting into Eq. (4.12), Ghonasgi and Chapman obtained SAFT-D equation as

$$Z^m = mZ^HS - \frac{m}{2} \left( 1 + \frac{\eta(5 - 2\eta)}{(1 - \eta)(2 - \eta)} \right) \left( \frac{m}{2} - 1 \right) \left( 1 + \frac{2\eta(2 + \eta)}{(1 - \eta)(1 + 2\eta)} \right) \quad (4.15)$$

In order to have accurate expression for $g_{HD}$ at all packing fractions, Ghonasgi and Chapman fit the high packing fraction results for $g_{HD}$ and obtained the following correlation for $g_{HD}$.

$$g_{HD}(\sigma) = \frac{1 + 2\eta + 26.45031\eta^{6.17}}{2(1 - \eta)^2} \quad (4.16)$$

This is in good agreement with simulations at high packing fractions. This correlation is obtained by adding a correction term to Chiew’s expression for $g_{HD}(\sigma)$ so that the agreement is good when compared to simulation results for packing fractions greater than 0.35. Using Eq.(4.16) in Eq.(4.12) takes the
form,

$$Z^m = mZ^{HS} - \frac{m}{2} \left( \frac{1 + \frac{\eta(5 - 2\eta)}{(1 - \eta)(2 - \eta)}}{\left( \frac{m}{2} - 1 \right)} \right)$$

$$\times \left[ 1 + \eta \left( \frac{2 + 163.1984\eta^{5.17}}{1 + 2\eta + 26.45031\eta^{6.17}} + \frac{2}{1 - \eta} \right) \right]$$

(4.17)

Equation (4.17) gives results for the compressibility factor which are in better agreement with simulation data high densities than equation (4.15). Equation (4.15) gives good results up to about a packing fraction of 0.35.

4.3 SADUS CORRECTIONS IN SAFT-D FOR LINEAR TANGENT CHAIN MOLECULES

Adopting the nomenclature of Chang and Sandler [16] Sadus will refer to Eqs. (4.15) as TPT-D1. Chang and Sandler also used a polynomial fit for the dimer site-site correlation function to obtain an alternative to Eqs.(4.15), which they called TPT-D2. The TPT-D2 equation can be represented as

$$Z^m = m \left( \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \right) - 0.5m \left( \frac{1 + \frac{\eta(5 - 2\eta)}{(1 - \eta)(2 - \eta)}}{1} \right)$$

$$- (0.5m - 1) \left( \frac{\eta(3.498 - 0.24\eta - 0.414\eta^2)}{(1 - \eta)(2 - \eta)(0.534 + 0.414\eta)} \right)$$

(4.18)

Comparison [16] with molecular simulation data indicates that both TPT-D1 and TPT-D2 represent the compressibility of 4-, 8-, and 16-mer hard-sphere chains more accurately than either the generalized Flory dimer (GF-D) equation or the original TPT equation of state. The predicted second virial coefficients are also in better agreement with molecular simulation data. In particular, the TPT-D1 equation
provides a reasonable representation of the asymptotic behaviour of the second virial coefficient for large hard-sphere chains.

The observation by Yethiraj and Hall [17] that the dimer site-site correlation function can be obtained as a linear function of the hard-sphere site-site correlation function suggested an easy simplification of Eqs.(4.12). In general, it can be define as,

\[ g_{HD} = g_{HS} (\alpha \eta + c) \]  

(4.19)

Substituting Eqs.(4.19) into Eqs.(4.12), Sadus obtained the equation as,

\[ Z^m = 1 + m(Z^{HS} - 1) + (1 - m) \eta \frac{\partial \ln g_{HS}}{\partial \eta} + \frac{\alpha \eta (2 - m)}{2(\alpha \eta + c)} \] 

(4.20)

Using Eqs.(4.20), the compressibility of the hard chain can be obtained directly from the hard-sphere properties and two unknown parameters, \( \alpha \) and \( c \). If the hard-sphere properties is used from Eqs.(4.6b) and (4.14), then the equation of state for the hard chain given by Eqs.(4.20) is

\[ Z^m = 1 + \frac{m(4 \eta - 2 \eta^2)}{(1 - \eta)^3} + (1 - m) \left( \frac{\eta(5 - \eta)}{(1 - \eta)(2 - \eta)} \right) + \frac{\alpha \eta (2 - m)}{2(\alpha \eta + c)} \]  

(4.21)

The values of \( \alpha \) and \( c \) can be obtained by fitting the molecular simulation data for \( g_{HS} \) and \( g_{HD} \). By fitting the simulation data for hard diatomic spheres, Yethiraj and Hall [17] found that \( c = 0.534 \). However, sadus propose an alternative approach which improves the accuracy of the equation of state. First, the value of \( c \) is determined by noting that when \( \eta = 0 \), the dimer site-site correlation function given by Eqs.(4.13) has a value of 0.5. The value of \( \alpha \) can be determined from the second virial coefficient. Sadus find that the average absolute deviation is minimized when \( \alpha = 0.7666 \). Consequently, Eqs.(4.21) becomes
\[ Z^m = 1 + \frac{m(4\eta - 2\eta^2)}{(1-\eta)^3} + \left(1 - m\right)\left(\frac{\eta(5 - \eta)}{(1-\eta)(2-\eta)}\right) + \frac{0.7666(2 - m)}{1.5332\eta + 1} \] (4.22)

This simplified thermodynamic perturbation theory-dimer equation referred as the STPT-D equation of state by Richard J. Sadus.

The compressibility predicted by the STPT-D equations of state is compared in Table 4.1 with molecular simulation data for hard chains containing 4, 8, 16, 32 hard-sphere segments. The simulation data for \( m \leq 16 \) and \( m = 32 \) were obtained from Chang and Sandler [16] and Denlinger and Hall [18] respectively.

The comparison in Table 4.1 also includes results for the generalized Flory dimer equation [19] (GF-D) and an equation of state based on a particle-particle description of chain proposed by Chiew [8].

The GF-D equation can be represented by

\[ Z_{GF-D} = \left(\frac{v_e(m) - v_e(1)}{v_e(2) - v_e(1)}\right)Z_{dimer} - \left(\frac{v_e(m) - v_e(2)}{v_e(2) - v_e(1)}\right)Z_{mono} \] (4.23)

\( v_e(m) \) is the excluded volume of a \( m \)-segment molecule calculated from

\[ v_e(m) \approx v_e(3) + (m - 2)(v_e(3) - v_e(2)) \] (4.24)

Where \( v_e(1) = 4\pi\sigma^3/3 \), \( v_e(2) = 9\pi\sigma^3/4 \), \( v_e(3) = 9.82605\sigma^3 \). The Carnahan-Starling [10] and Tildesley-Streelt [20] equations were used for the compressibility of the monomer and dimer respectively. Chiew’s [8] expression for an \( m \)-segment hard chain can be written as

\[ Z^m = m + g_{HS}(\sigma)\{m(4\eta - 1) + 1\} \] (4.25)

and when \( g_{HS} \) is calculated from Eqs.(4.13). The Chiew’s equation can be represented by
\[ Z^m = m + \frac{\{m(4\eta - 1) + 1\}(2 - \eta)}{2(1 - \eta)^3} \]  

(4.26)

Equation (4.26), which will we refer to as Chiew’s equation is of particular interest because it forms the basis of state for polymers.

Table 4.1. Comparisons of Molecular Simulation Data [16, 18, 11] with equation of state calculations for compressibility of m-hard-sphere chains as a function of reduced density (\(\rho^* = m\rho\sigma^3\))

<table>
<thead>
<tr>
<th>(\rho^*)</th>
<th>Simulation</th>
<th>Chiew</th>
<th>GFD</th>
<th>TPT-D1</th>
<th>TPT-D2</th>
<th>STPT-D</th>
<th>Eq.(4.35) (ours)</th>
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</tr>
<tr>
<td>0.1</td>
<td>2.25</td>
<td>2.67</td>
<td>2.67</td>
<td>2.29</td>
<td>2.48</td>
<td>2.23</td>
<td>2.21</td>
</tr>
<tr>
<td>0.2</td>
<td>4.47</td>
<td>5.04</td>
<td>5.24</td>
<td>4.64</td>
<td>4.89</td>
<td>4.45</td>
<td>4.39</td>
</tr>
<tr>
<td>0.3</td>
<td>8.09</td>
<td>8.39</td>
<td>9.06</td>
<td>8.39</td>
<td>8.60</td>
<td>8.00</td>
<td>8.09</td>
</tr>
<tr>
<td>0.5</td>
<td>21.96</td>
<td>19.79</td>
<td>22.77</td>
<td>22.52</td>
<td>22.32</td>
<td>21.49</td>
<td>22.17</td>
</tr>
<tr>
<td>0.6</td>
<td>34.05</td>
<td>29.34</td>
<td>34.59</td>
<td>34.92</td>
<td>34.35</td>
<td>33.44</td>
<td>34.56</td>
</tr>
<tr>
<td>m=32</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>0.191</td>
<td>7.08</td>
<td>8.28</td>
<td>8.62</td>
<td>7.36</td>
<td>7.90</td>
<td>6.99</td>
<td>6.73</td>
</tr>
<tr>
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<td>25.26</td>
<td>24.00</td>
<td>24.18</td>
<td>22.68</td>
<td>23.15</td>
</tr>
<tr>
<td>0.478</td>
<td>37.0</td>
<td>34.15</td>
<td>39.47</td>
<td>38.75</td>
<td>38.46</td>
<td>36.74</td>
<td>37.80</td>
</tr>
</tbody>
</table>

161
The relative simplicity of Chiew’s equation makes it very attractive for computationally intensive applications such as phase equilibria. Song et al. [21,22] have demonstrated that it can be formulated into a useful equation of state for polymers. However, the data in Table (4.1) clearly indicate the Chiew’s equation is not very accurate. It provides a reasonable prediction of the compressibility only at low densities, and the discrepancy with simulation data increases substantially with chain length. The GFD equation adequately predicts the compressibility at all densities, but it becomes progressively less accurate as the number of hard-sphere segments in the chain is increased. For \( m \geq 32 \) it tends to overpredict the compressibility at both low and very high densities.

4.4. MODIFIED STATISTICAL ASSOCIATING FLUID-DIMER THEORY

FOR LINEAR TANGENT CHAIN MOLECULES

We have re-examined that equation of state SAFT-D theory. The theory employed the contact value of the correlation function \( g(\sigma) \) of the multimer proposed by Chiew [8]. Who has derived two analytical expressions for the average correlation function at contact as a function of chain length \( m \) and hard sphere site volume\( \eta \). Ghonasgi and Chapman [7] have employed the expression \( g(\sigma) \) of dimer with an assumption that the correlation function at contact of the dimer, tetramer, octamer and so on will remain the same. We have applied both the expressions for \( g(\sigma) \) for \( m \)-components separately without making assumption.

Let us consider even numbered pairs of \( m \) hard spheres. The equation of
state of the disphere in SAFT theory can be written as

\[ Z^{HD} = 2Z^{HS} - \left( 1 + \eta \frac{\partial \ln g_{HS}(\sigma)}{\partial \eta} \right) \]  

(4.27)

Where \( \eta \) is the packing fraction or volume fraction and is defined as \( \eta = \pi \rho m \sigma^3 / 6 \).

The pair of disphere can form a chain which has four segments i.e. tetramers, In SAFT-D theory [7], the equation of state for a tetramer is given by

\[ Z^{HT} = 2Z^{HD} - \left( 1 + \eta \frac{\partial \ln g_{HD}(\sigma)}{\partial \eta} \right) \] 

(4.28)

Similar, the equations of state of 8 mers \((Z^{HO})\), 16 mers \((Z^{HSix})\), and 32 mers \((Z^{32})\), and so on can be written as

\[ Z^{HO} = 2Z^{HT} - \left( 1 + \eta \frac{\partial \ln g_{HT}(\sigma)}{\partial \eta} \right) \] 

(4.29)

\[ Z^{HSix} = 2Z^{HO} - \left( 1 + \eta \frac{\partial \ln g_{HO}(\sigma)}{\partial \eta} \right) \] 

(4.30)

\[ Z^{32} = 2Z^{HSix} - \left( 1 + \eta \frac{\partial \ln g_{HSix}(\sigma)}{\partial \eta} \right) \] 

(4.31)

The equation of state for 128 mers can be solved as
\[ Z^{128} = 128 Z^{HS} - 64 \left( 1 + \eta \frac{\partial \ln g_{HS}(\sigma)}{\partial \eta} \right) - 32 \left( 1 + \eta \frac{\partial \ln g_{HD}(\sigma)}{\partial \eta} \right) \]
\[ -16 \left( 1 + \eta \frac{\partial \ln g_{HT}(\sigma)}{\partial \eta} \right) - 8 \left( 1 + \eta \frac{\partial \ln g_{HO}(\sigma)}{\partial \eta} \right) - 4 \left( 1 + \eta \frac{\partial \ln g_{HSix}(\sigma)}{\partial \eta} \right) \]
\[ -2 \left( 1 + \eta \frac{\partial \ln g_{H2}(\sigma)}{\partial \eta} \right) - 1 \left( 1 + \eta \frac{\partial \ln g_{H64}(\sigma)}{\partial \eta} \right) \]

(4.32)

A general expression can be written as

\[ Z^m = mZ^{HS} - (m - 1) - \eta \left\{ \frac{m \ln g_{HS}(\sigma)}{2} \frac{\partial \ln g_{HS}(\sigma)}{\partial \eta} + \frac{m \ln g_{HD}(\sigma)}{4} \frac{\partial \ln g_{HD}(\sigma)}{\partial \eta} \right. \]
\[ + \frac{m \ln g_{HT}(\sigma)}{8} \frac{\partial \ln g_{HT}(\sigma)}{\partial \eta} + \frac{m \ln g_{HO}(\sigma)}{16} \frac{\partial \ln g_{HO}(\sigma)}{\partial \eta} + \frac{m \ln g_{HSix}(\sigma)}{32} \frac{\partial \ln g_{HSix}(\sigma)}{\partial \eta} \]
\[ + \frac{m \ln g_{H2}(\sigma)}{64} \frac{\partial \ln g_{H2}(\sigma)}{\partial \eta} + \frac{m \ln g_{H64}(\sigma)}{128} \frac{\partial \ln g_{H64}(\sigma)}{\partial \eta} \right\} \]

(4.33)

Equation (4.33) can be solved by using the value of \( g_m(\sigma) \) proposed by Chiew [8] as

\[ g_m(\sigma) = \frac{(m + 2) + (5m - 2)\eta}{4m(1 - \eta)^2} \]

(4.34)

The equation of state (eq. 4.33) can further be solved as

\[ Z^m = mZ^{HS} - (m - 1) - \left( \frac{\eta}{1 - \eta} \right) \left\{ \frac{m}{2} \frac{5 - 2\eta}{(2 - \eta)} + \frac{m}{4} \frac{2 + \eta}{1 + 2\eta} \right. \]
\[ + \frac{m}{8} \frac{5 + 3\eta}{(1 + 3\eta)} + \frac{m}{16} \frac{29 + 19\eta}{(5 + 19\eta)} + \frac{m}{32} \frac{57 + 39\eta}{(9 + 39\eta)} \]
\[ + \frac{m}{64} \frac{113 + 79\eta}{(17 + 79\eta)} + \frac{m}{128} \frac{193 + 160\eta}{(33 + 160\eta)} \right\} \]

(4.35)
The equation of state for 4 mers, 8 mers and 16 mers can be written by taking into account the terms up to $\frac{m}{x} = 1$. However, this way we can obtain the equations of state for 32 mers, 64 mers and 128 mers etc. but not for the 51 mers and 201 mers for which simulation results are available. We have obtained the equation of state of 50 mers and 200 mers by adding its segmental chain's equations of state. Thus, the EOS of 50 mers is obtained by adding EOS of 32 mers, 16 mers, 2 mers and the EOS of 200 mers is obtained by adding EOS of 128 mers, 64 mers and 8 mers. The equation of state of 50 mers and 200 mers can be written as

$$Z(50) = Z(32) + Z(16) + Z(2), \quad (4.36a)$$

and

$$Z(200) = Z(128) + Z(64) + Z(8). \quad (4.36b)$$

For comparison, we have also calculated the equation of state of 50 mers and 200 mers by the equation of state proposed by Ghonasgi and Chapman [7] derived by assuming that longer chains have same density dependence of the site-site correlation function $g_m(\sigma)$ as the disphere $g_{HD}(\sigma)$. The equation of state [7] is given by

$$Z^n = mZ_{\text{HS}} - \frac{m}{2} \left( 1 + \frac{\eta(5 - 2\eta)}{(1 - \eta)(2 - \eta)} \right) - \left( \frac{m}{2} - 1 \right) \left( 1 + \frac{2\eta(2 + \eta)}{(1 - \eta)(1 + 2\eta)} \right) \quad (4.37)$$
4.5. RESULTS AND DISCUSSION FOR HOMONUCLEAR HARD SPHERE

TANGENT LONG CHAIN MOLECULES

The equations of state of long chain molecules having 50mers and 200mers are calculated by using equation (4.36a,b) and tabulated in table 4.2 and table 4.3. The predicted values are compared with molecular simulation data [11] as well as with results obtained by using equation (4.37). We find that the present work predicts a better agreement with simulation data than those obtained by equation (4.37) proposed by Ghonasgi and Chapman [7]. This means that the density dependence of the site-site correlation function at contact for higher mers plays an important role in describing the equation of state for long chains. Thus, we have obtained the equation of state of 50 mers and 200 mers by the addition of equations of state of its segments. This describes the possibility of addition or subtraction of equations of state of the segments of the chain molecules.

We have also compared our equation of SAFT-D system with other equations of state (discussed in chapter-4(4.3)) in table 4.1. We find that our equation of state presents better results and more close to simulation results than other equation of state.
Table 4.2: Comparison of our equation of state of 50 mers hard sphere chain fluids with equation (4.37) and with simulation data [11] as a function of reduced density ($\rho^* = m\rho\sigma^3 = 6\eta/\pi$).

<table>
<thead>
<tr>
<th>$\rho^*$</th>
<th>Present Work</th>
<th>Eq. (4.36a)</th>
<th>Eq. (4.37)</th>
<th>Simulation Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>7.2387</td>
<td>4.3924</td>
<td>1.810</td>
<td>13.441</td>
</tr>
<tr>
<td>0.3</td>
<td>14.1468</td>
<td>8.0972</td>
<td>2.4584</td>
<td>24.7024</td>
</tr>
<tr>
<td>0.372</td>
<td>21.9350</td>
<td>11.9382</td>
<td>3.0743</td>
<td>36.9475</td>
</tr>
<tr>
<td>0.464</td>
<td>35.3716</td>
<td>18.7631</td>
<td>3.3984</td>
<td>57.5331</td>
</tr>
<tr>
<td>0.590</td>
<td>63.7252</td>
<td>33.0958</td>
<td>6.1669</td>
<td>102.9879</td>
</tr>
<tr>
<td>0.649</td>
<td>82.6298</td>
<td>42.6274</td>
<td>7.4949</td>
<td>132.7521</td>
</tr>
<tr>
<td>0.7</td>
<td>102.931</td>
<td>52.8509</td>
<td>8.8983</td>
<td>164.6803</td>
</tr>
<tr>
<td>0.8</td>
<td>157.258</td>
<td>80.1723</td>
<td>12.5837</td>
<td>250.0142</td>
</tr>
<tr>
<td>0.9</td>
<td>240.114</td>
<td>121.784</td>
<td>18.0960</td>
<td>379.9947</td>
</tr>
</tbody>
</table>
Table 4.3: Comparison of our equation of state of 200 mers hard sphere chain fluids with equation (4.37) and with simulation data [11] as a function of reduced density ($\rho^* = m \rho \sigma^3 = 6\eta/\pi$).

<table>
<thead>
<tr>
<th>$\rho^*$</th>
<th>Present Work</th>
<th>Eq. (4.36b)</th>
<th>Eq. (4.37)</th>
<th>Simulation Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>128 mers</td>
<td>64 mers</td>
<td>8 mers</td>
<td>= 200 mers</td>
</tr>
<tr>
<td>0.2</td>
<td>24.34</td>
<td>12.96</td>
<td>2.96</td>
<td>40.26</td>
</tr>
<tr>
<td>0.3</td>
<td>52.37</td>
<td>27.04</td>
<td>4.92</td>
<td>84.33</td>
</tr>
<tr>
<td>0.4</td>
<td>96.11</td>
<td>49.00</td>
<td>7.86</td>
<td>152.97</td>
</tr>
<tr>
<td>0.5</td>
<td>161.80</td>
<td>81.95</td>
<td>12.19</td>
<td>255.94</td>
</tr>
<tr>
<td>0.6</td>
<td>259.16</td>
<td>130.74</td>
<td>18.51</td>
<td>408.41</td>
</tr>
<tr>
<td>0.7</td>
<td>403.56</td>
<td>203.07</td>
<td>27.79</td>
<td>634.42</td>
</tr>
<tr>
<td>0.8</td>
<td>619.95</td>
<td>311.41</td>
<td>41.61</td>
<td>972.97</td>
</tr>
<tr>
<td>0.9</td>
<td>950.31</td>
<td>476.76</td>
<td>62.60</td>
<td>1489.67</td>
</tr>
</tbody>
</table>
4.6. FUSED HARD-SPHERE CHAIN MOLECULES

The fused hard-sphere (FHS) chain model which allows overlap between adjacent hard-sphere monomers along a chain is one step closer than the tangent hard-sphere chain model to realistic polymer chains such as alkanes and polyethylene where the bond length to monomer diameter ratio is around 0.4 [23, 24]. The equation of state for FHS chains, however, is not as well developed as for tangent hard-sphere chain fluids and can not be applied directly to FHS chain fluid.

Several attempts have been made to extend TPT1 expressions to FHS chain fluids. One of the models is to relate the effective chain length to the scale-particle theory (SPT) parameter $\alpha$ at the second virial coefficient level [24, 25]. This method yields virial coefficient [24, 25, 26]. Amos and Jackson [27] suggested replacing the FHS molecule with an ‘equivalent’ tangent hard-sphere molecule, but the method is limited to small FHS molecules. Jackson and Gubbins [28] and Phan et al. [29] used interpolation schemes to extend TPT1 expressions to FHS chain fluids, but the accuracy of the resulting compressibility factors deteriorates rapidly as the chain length increases [29].

While various methods have been used in extending TPT1 to FHS chain fluids, the extension of the GF theories to such fluids to focus on finding appropriate reference fluids. The GF approach is based on the idea that the compressibility factor of long chain molecules can be obtained from knowledge of the compressibility of shortest chain fluids, e.g., monomer and dimer fluids, which are, in effect reference fluids. Honnell and Hall [5] proposed an approximation A in which the diameters of the underlying reference monomer and fused dimer fluid are taken to be identical to those of the FHS chain, but the number of beads per unit volume of the monomer and
dimer fluids are adjusted to make their volume fractions identical to the volume fraction of the FHS chain fluid. Yethiraj et al. [17] developed an approximation B in which the number of beads per unit volume of the underlying reference monomer and fused dimer and bond length of the underlying fused dimers are taken to be identical to that of the FHS chain, but the diameters of the underlying monomers and fused dimers are adjusted in such a way that the volume faction is the same as that of the FHS chain fluid. Recently, Costa et al. [30] further refined the reference monomer and dimer fluids to yield GF-AB, GFD-AB and GFD-AC theories. They found that the GF-AB and GFD-AC theories provided more accurate prediction for the compressibility factors of the FHS chain fluids than either the GF or the GFD versions of approximations A or approximation B.

4.7. EQUATIONS OF STATE OF LINEAR FUSED HARD SPHERE (LFHS) CHAIN FLUIDS

The equation of state of LTHS chain fluids obtained by using SAFT-D theory (Eq. 4.35) can be transformed into the equation of state of LFHS chain fluids by considering the suitable value of chain length i.e. by replacing \( m \) by considering the correct chain length \( (m^*) \). This is shown by considering equations of state of 4 mers, 8 mers and 16 mers for which simulation results are available. The validity of the proposed method remains true for the equations of state derived by other theoretical methods. To show this, we have considered the following equations of state.

(i) TPT-D2 equation of state for LTHS chain fluids proposed by Chang and
Sandler [16] as

\[ Z = m Z_{HS} - 0.5m \left( 1 + \frac{\eta (5 - 2\eta)}{(1 - \eta)(2 - \eta)} \right) \]
\[ - (0.5m - 1) \left( 1 + \frac{\eta (3.498 - 0.24\eta - 0.414\eta^2)}{(1 - \eta)(2 - \eta)(.534 + 0.414\eta)} \right) \] (4.38)

(ii) Equation of state for LTHS chain fluids through r-particle cavity correlation function for chain by HU et al. [31] as

\[ \frac{\beta P}{\rho} = Z = \frac{1 + a\eta + b\eta^2 + c\eta^3}{(1 - \eta)^3} \] (4.39)

where \( a, b \) and \( c \) are functions of chain length \( m \) given in their paper by equations (33-35).

(iii) Quartic optimized chain SAFT equation of state for LTHS chain fluids proposed by Yelash and Kraska [32] as

\[ Z_{BOCK} = 1 + m \frac{2\eta (6 + \eta)}{(1 - \eta)(3 - 4\eta)} - m \frac{a}{bRT} \frac{4\eta + (m - 1)37\eta^2 - 30\eta}{4(1 - \eta)(3 - 4\eta)} \] (4.40)

where \( \frac{a}{bRT} \) is assumed to be a constant value. It is obtained by fitting the equation of state to its MC simulation value at respective \( \eta \) for 8 mers. The average value of all these values at different \( \eta \) is found as \( \frac{a}{bRT} = 0.0615 \). The value of \( \frac{a}{bRT} \) is small so it will not make much effect on the equation of state by considering it as a constant.
4.8. **EVALUATION OF EFFECTIVE CHAIN LENGTH m***

To transform an equation of state of LTHS chain into an equation of state of LFHS chain, we adjust the number of beads per unit volume so that the reference dimer fluids have the same volume fraction and the same surface area as the fused hard sphere chain. The effective number of dimers per chain is taken as m* and the dimer diameter is d. Thus the volume (V_m) and surface area (S_m) of a fused hard sphere chain can be written as

\[
V_m = m^* \frac{\pi d^3}{6} \left[1 + \frac{3}{2} \left(\frac{\ell}{d}\right) - \frac{1}{2} \left(\frac{\ell}{d}\right)^3\right]
\]

(4.41a)

\[
S_m = m^* \pi d^2 \left[1 + \left(\frac{\ell}{d}\right)\right]
\]

(4.41b)

and we can obtain the value of m* using equations (4.41a) and (4.41b)

\[
m^* = \left(\frac{S_m^3}{36\pi V_m^2}\right) \left[1 + \frac{3}{2} \left(\frac{\ell}{d}\right) - \frac{1}{2} \left(\frac{\ell}{d}\right)^3\right]^2 \left[1 + \left(\frac{\ell}{d}\right)\right]^{-3}
\]

(4.42)

Thus the effective chain length (m*) of the fused hard sphere chain can be obtained where V_m and S_m are known from Monte Carlo simulation results. Costa et al. [30] have tabulated the values of V_m and S_m for 4 mers, 8 mers and 16 mers at \(\ell^* = 0.3\).

Whittle and Masters [33] have used the Monte Carlo method to study the
three systems of fused hard spheres of 8 mers at $\ell^* = 0.5$, 8 mers at $\ell^* = 0.6$ and 6 mers at $\ell^* = 0.5$. They have reported the molecular volume at respective length to width ratio $\ell^*$. Since the value of $S_m$ is not known, we can not use equation (4.42) to determine the value of $m^*$. We use the following procedure to obtain $m^*$.

Let us consider a chain of $(2m-1)$ overlapping spheres of radius $d$ and volume $V_s = 4\pi d^3/3$ separated by the $m$ mer of bond length $\ell^*$. The excluded volume is given by the relation.

$$V_m(o) = (2m-1)V_s - 2(m-1)V_o$$ (4.43)

where the overlap volume between a pair of adjacent sphere $V_o$ is given by [34]

$$V_o = \frac{4\pi d^3}{3} \left[ 1 - \frac{3}{4} \left( \frac{\ell}{d} \right) - \frac{1}{16} \left( \frac{\ell}{d} \right)^3 \right]$$ (4.44)

Further

$$V_m(o) = 8 V_{sc}$$ (4.45)

Here $V_{sc}$ is the spherocylinder molecular volume, tabulated by Whittle and Masters [33]. Thus equation (4.43) can be written as

$$8 V_{sc} = (2m-1) \frac{4\pi d^3}{3} - 2(m-1) \frac{4\pi d^3}{3} \left[ 1 - \frac{3}{4} \left( \frac{\ell}{d} \right) - \frac{1}{16} \left( \frac{\ell}{d} \right)^3 \right]$$ (4.46)
We determine the value of $d$ by using equation (4.46). Now, the fused hard spheres can be approximated [33, 34] by a spherocylinder such that the volume of the spherocylinder is equal to the volume of a single FHS chain molecule ($m$-mers) i.e. $V_{sc} = V_m$. Thus, knowing the value of $d$ from equation (4.46) and considering $V_{sc} = V_m$, we can determine the value of $m^*$ by using equation (4.41a) for $8$ mers.

Recently, we [35] have proposed an equation of state for LTHS chain molecules using the statistical associating fluid theory (SAFT). The formalism is based on the assumption that the chain is formed by the pairs of the trimers. Following this assumption, the equation of state of the LTHS six mers chain is given by

$$Z^m = mZ^{1s} - (m-1)(m-2)\frac{\eta}{1-\eta}\left(\frac{5-2\eta}{2-\eta}\right) - \frac{\eta}{1-\eta}\left(\frac{23+13\eta}{5+13\eta}\right)$$

(4.47)

where $m = 6$ represents the chain length in this case. The volume of a chain of $m$ mers formed by the pairs of the LTHS trimer is given by

$$V_m = m\frac{\pi d^3}{6}\left[1 + 3\left(\frac{\ell}{d}\right) - \left(\frac{\ell}{d}\right)^3\right]$$

(4.48)

Now, equation (4.48) can be used to calculate the effective chain length $m^*$ for LFHS chain fluids by replacing $m$ by $m^*$. The value of the diameter $d$ can be calculated using equation (4.43). $V_m$ for six mers is known from Whittle and Masters [33]. The equation of state of the LFHS chain of six mers fluids at $\ell^* = 0.5$ can be obtained from equation (4.47) by replacing $m$ by $m^*$ at
different volume fractions.

4.9 RESULTS AND DISCUSSION FOR LINEAR FUSED HARD SPHERE (LFHS) CHAIN MOLECULES

We have applied SAFT-D theory (eq. 4.35) and other equations of state described by equations (4.38) to (4.40) of tangent hard sphere chain molecules to predict the equations of state of linear fused hard sphere chain fluids. To apply these theories to LFHS chain fluid, the effective number of dimer per chain \( m^* \) is calculated using equation (4.42) for 4 mers, 8 mers and 16 mers. The value of \( m^* \) for respective mers is calculated using the parameters tabulated in table 4.4 and the same value of \( m^* \) is used for all four equations of state. The calculated values of equations of state for LFHS chain of 4 mers, 8 mers and 16 mers are shown in figure 4.1. We find that the compressibility factor is tremendously reduced for LFHS chain fluids in comparison to LTHS chain fluids. Further, all four equations of state of LFHS chain fluids, considered in the present work, adequately predict the compressibility factor in agreement with MC simulations [11] and dispose almost same values of compressibility factor \( (Z^m) \) by using the same value of \( m^* \). Figure 4.1 also reveals that all four equations of state including SAFT-D underpredict the compressibility factor compared with simulation results. This discrepancy is almost negligible for 4 mers but increases with chain length, i.e., for 8 mers and 16 mers.

Now, we describe the equations of state of fused hard sphere chain fluids of 8 mers at length to width ratio \( \ell^* = 0.5 \) and \( \ell^* = 0.6 \). In this case, the value of
m* is calculated by using equation (4.46) and equation (4.41a) as described in the last section 4.8. The results for the SAFT-D theory using equation (4.35) are shown in figures 4.2 at $\ell^* = 0.5$ and $\ell^* = 0.6$. The equation of state at $\ell^* = 0.5$ shows a good agreement with simulation data up to the volume fraction $\eta = 0.3$ above which it is closer to the modified Wertheim equation (MW) of state data [36] and predicts higher values than GFD theory. However, there is a possibility of mild phase transition above $\eta = 0.4$. Our equation of state at $\ell^* = 0.6$ predicts good agreements with Monte Carlo data up to volume fraction $\eta = 0.33$ which is the density at which Whittle and Master [33] identify an isotropic/nematic phase transition. The equation of state of 6 mers i.e. equation (4.47), shows an excellent agreement with simulation data for full density range. LFHS of 6 mers with $\ell^* = 0.5$ do not show clear phase transition by using GFD theory [36] and modified Parsons-Lee theory [37] as well. The results are shown in figure 4.3.

4.10. SECOND VIRIAL COEFFICIENT ($B_2$)

The second virial coefficient depends upon the intermolecular pair potential and is also a function of temperature. Thus it summarizes the influence of two body interactions on the pressure. The second virial coefficient for tangent hard sphere chain molecules is given by the well-known expression.

$$B^*_2 = \frac{B_2}{V_m} = \frac{1}{2}(3m + 5)$$ (4.49)

As shown in table 4.5, the second virial coefficient of LTHS chain predicted by equation (4.49) is in reasonably good agreement with Monte carlo simulation
data [38]. We show that equation (4.49) also predicts good agreement with MC simulation results [38] for linear fused hard sphere chain fluids using our values of effective chain length $m^*$. The MC simulation results of 6 mers and 8 mers LFHS chain are obtained by considering the mean value of 5, 7 and 9 mers MC simulation results [38].

Table 4.4: parameters used in the calculations of fused hard sphere chain fluids obtained from Costa et al. [30] and Whittle and Masters [33]

<table>
<thead>
<tr>
<th>Mers</th>
<th>$\ell^*$</th>
<th>$V_m$</th>
<th>$S_m$</th>
<th>d</th>
<th>$m^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.3664</td>
<td>1.422</td>
<td>6.905</td>
<td>-</td>
<td>1.311</td>
</tr>
<tr>
<td>6</td>
<td>0.50</td>
<td>2.323</td>
<td>-</td>
<td>0.9829</td>
<td>1.967</td>
</tr>
<tr>
<td>8</td>
<td>0.3330</td>
<td>2.575</td>
<td>11.728</td>
<td>-</td>
<td>1.992</td>
</tr>
<tr>
<td>8</td>
<td>0.50</td>
<td>3.043</td>
<td>-</td>
<td>0.9818</td>
<td>3.639</td>
</tr>
<tr>
<td>8</td>
<td>0.60</td>
<td>3.426</td>
<td>-</td>
<td>0.9726</td>
<td>3.968</td>
</tr>
<tr>
<td>16</td>
<td>0.3195</td>
<td>4.920</td>
<td>21.547</td>
<td>-</td>
<td>3.404</td>
</tr>
</tbody>
</table>
Table 4.5. Reduced second virial coefficient ($B^*_2$) for linear tangent hard sphere chains and linear fused hard sphere chains using equation (4.48).

<table>
<thead>
<tr>
<th></th>
<th>LTHS</th>
<th></th>
<th>LFHS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$m$</td>
<td>$\ell^*$</td>
<td>$B^*_2$ (Th)</td>
<td>$B^*_2$ (MC)</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>8.5</td>
<td>8.25</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>11.5</td>
<td>11.03</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>14.5</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.1: Compressibility factor versus volume fraction for 4 mers, 8 mers and 16 mers: our values (SAFT-D theory) solid line (——), Reference 31 (-- - - - --), Reference 32 (--- - - - -), Reference 16 (-x--x--x--), MC values (circles).
Figure 4.2: Compressibility factor versus volume fraction for linear fused hard sphere 8mers with $\ell^* = 0.5$ and $\ell^* = 0.6$. Our values (SAFT-D) theory) solid line (-----), GFD (- - -) modified Wertheim equation (- - - -), Monte Carlo simulation data (circles).
Figure 4.3: Compressibility factor versus volume fraction for linear fused hard sphere 6mers with $\ell^* = 0.5$, our values (SAFT-D Theory) solid line(-----), GFD (- . - . -) modified Wertheim equation (- - - -), Monte Carlo simulation data (circles).
4.11 REFERENCES


