CHAPTER – 6

EQUATION OF STATE OF TANGENT HARD SPHERE AND FUSED HARD SPHERE CHAIN FLUIDS

CONTENTS

6.1 INTRODUCTION

6.2 SIMPLIFIED TPT HARD-CHAIN EQUATION OF STATE

6.3 FORMULATION OF EOS FOR TANGENT HARD SPHERE CHAIN FLUIDS

6.4 RESULTS AND DISCUSSION FOR HOMONUCLEAR HARD SPHERE TANGENT CHAIN MOLECULES

6.5 FUSED HARD SPHERE CHAIN MOLECULES

6.6 FORMULATION OF EFFECTIVE CHAIN LENGTH FOR FUSED HARD SPHERE CHAINS

6.7 RESULTS AND DISCUSSION OF EOS FOR FUSED HARD SPHERE CHAIN MOLECULES

6.8 REFERENCES
The tangent hard sphere chain model has attracted wide-spread attention because it takes into account two important features of a 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 pearly-necklace model can play a 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. Though, 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. 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. In this chapter, we have applied both the expressions for $g(\sigma)$ for $m$ components separately without making any assumption. We have found that the equations of state obtained by using both the expressions for $g(\sigma)$ predict better results than those obtained by Ghonasgi and Chapman. The theory has been applied to tangent hard sphere chains and also to fused hard sphere linear chains. Considering the correct value of the chain length $m^*$, SAFT-D theory predicts good values for the compressibility factor fused hard sphere chain molecules. The SAFT-D theory describes better equation of state in comparison to GFD theory for longer chain molecules.
6.2 SIMPLIFIED TPT HARD-CHAIN EQUATION OF STATE

Chapman et al. [6, 7] have generalized Wertheim’s TPT model to obtain the following equation of state for the compressibility \((Z)\) of a hard-chain of \(m\) segments:

\[
Z^{(HC)} = mZ^{HS} - (m-1)\left(1 + \eta \frac{\partial \ln g_{HS}(\sigma)}{\partial \eta}\right) \tag{6.1}
\]

where \(g_{HS}(\sigma)\) is the hard-sphere site-site correlation function at contact, \(\sigma\) is the hard-sphere diameter, \(\eta = \pi m \rho \sigma^3 / 6\) is the packing fraction, and \(\rho\) is the number density. The compressibility of hard spheres \((Z^{HS})\) can be accurately determined from the Carnahan-Starling (CS) equation:

\[
Z^{CS} = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3} \tag{6.2}
\]

For the Carnahan-Starling equation, the site-site correlation function is

\[
g_{HS}(\sigma) = \frac{2 + \eta}{2(1-\eta)^3} \tag{6.3}
\]

Recently, Ghorasgi and Chapman [7] and Chang and Sandler [9] modified TPT for the hard-sphere chain by incorporating structural information for the diatomic fluid. The compressibility of a hard chain can be determined from the hard-sphere compressibility and the site-site correlation function at contact of both hard spheres and hard dimers \((g_{HD})\).
\[ Z^m = mZ^{HS} - 0.5m \left( 1 + \eta \frac{\partial \ln g_{HS}(\sigma)}{\partial \eta} \right) - (0.5m - 1) \left( 1 + \eta \frac{\partial \ln g_{HD}(\sigma)}{\partial \eta} \right) \] (6.4)

Chiew [8] has obtained the site-site correlation for dimers:

\[ g_{HD}(\sigma) = \frac{1 + 2\eta}{2(1 - \eta)^2} \] (6.5)

If eqs. 6.2, 6.3 and 6.5 are substituted into eq. 6.4, then the resulting equation of state is

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

\[ - (0.5m - 1) \left( 1 + \frac{2\eta(2 + \eta)}{(1 - \eta)(1 + 2\eta)} \right) \] (6.6)

Adopting the nomenclature of Chang and Sandler [9] we will refer to eq. (6.6) as TPT-D1. Chang and Sandler also used a polynomial fit for the dimer site-site correlation function to obtain an alternative to eq. (6.6), which they called TPT-D2. The TPT-D2 equation can be represented as

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

\[ - (0.5m - 1) \left( 1 + \frac{\eta \left( 3.498 - 0.24\eta - 0.414\eta^2 \right)}{(1 - \eta)(2 - \eta)(0.534 + 0.414\eta)} \right) \] (6.7)

Comparison [9] 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 behavior of the second virial coefficient for large hard-sphere chains.

The observation by Yethiraj and Hall [10] that the dimer site-site correlation function can be obtained as a linear function of the hard-sphere site-site correlation function suggests an easy simplification of eq. (6.4). In general, we define

$$g_{\text{HD}} = g_{\text{HS}}(\alpha \eta + c)$$  \hspace{1cm} (6.8)

Substituting eq. (6.8) into eq. (6.4), we obtain

$$Z^m = 1 + m(Z^{\text{HS}} - 1) + (1 - m)\eta \frac{\partial \ln g_{\text{HS}}}{\partial \eta} + \frac{\alpha \eta(2 - m)}{2(\alpha \eta + c)}$$  \hspace{1cm} (6.9)

Using eq. (6.9), the compressibility of the hard chain can be obtained directly from the hard-sphere properties and two unknown parameters, $\alpha$ and $c$. If we obtain the hard-sphere properties from eqs. (6.2) and (6.3), then the equation of state for the hard chain given by eq. (6.9) is

$$Z^m = 1 + \frac{m(4\eta - 2\eta^2)}{(1 - \eta)^3} + (1 - m) \left( \frac{\eta(5 - \eta)}{(1 - \eta)(2 - \eta)} \right) + \frac{\alpha \eta(2 - m)}{2(\alpha \eta + c)}$$  \hspace{1cm} (6.10)
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 [10] found that $c = 0.534$. However, we 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 eq. (6.5) has a value of 0.5. If we choose $c = 0.5$ then eq. (6.8) will also yield a limiting value of 0.5. The value of $\alpha$ can be determined from the second virial coefficient. We find that the average absolute deviation is minimized when $\alpha = 0.7666$. Consequently, eq. (6.10) becomes

$$Z^m = 1 + \frac{m(4\eta - 2\eta^2)}{(1-\eta)^3} + (1 - m)\left(\frac{\eta(5 - \eta)}{(1 - \eta)(2 - \eta)}\right) + \frac{0.7666(2 - m)}{1.5332\eta + 1}$$

(6.11)

We will refer to this simplified thermodynamic perturbation theory-dimer equation as the STPT-D equation of state.

The compressibility predicted by the STPT-D equation and other equations of state is compared in Table 6.3 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 [9] and Denlinger and Hall [11] respectively.

The comparison in Table 6.3 also includes results for the generalized Flory dimer equation [12] (GF-D) and an equation of state based on a particle-particle description of chain proposed by Chiew [4]. The GF-D
equation can be represented by

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

(6.12)

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

\[ v_e(m) = v_e(3) + (m-2)(v_e(3) - v_e(2)) \]  

(6.13)

where \( v_e(1) = 4\pi a^3 / 3 \), \( v_e(2) = 9\pi a^3 / 4 \), \( v_e(3) = 9.82605\sigma^3 \). The Carnahan-Starling [13] and Tildesley-Streett [14] equations were used for the compressibility of the monomer and dimer respectively. Chiew's [4] expression for an \( m \)-segment hard chain can be written as

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

(6.14)

and when \( g_{\text{HS}} \) is calculated from eq. (6.3), we obtain

\[ Z^m = m + \frac{(m(4\eta - 1) + 1)(2 - \eta)}{2(1 - \eta)^3} \]  

(6.15)

Equation (6.15), which will we refer to as Chiew's equation is of particular interest because it forms the basis of equation of state for polymers.

The relative simplicity of Chiew's equation makes it very attractive for computationally intensive applications such as phase equilibria. Song et al. [15] have demonstrated that it can be formulated into a useful equation of state for polymers. However, the data in Table (6.3) 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 GF-D 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.

6.3 FORMULATION OF EOS FOR TANGENT HARD SPHERE CHAIN FLUIDS

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

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

(6.16)

The pair of dispheres 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

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

(6.17)

Similarly, the equations of state of 8-mers \( (Z^{\text{HO}}) \), 16-mers \( (Z^{\text{HSix}}) \) and 32-mers \( (Z^{32}) \) can be written as
\[
Z^{\text{HO}} = 2Z^{\text{HT}} - \left(1 + \eta \frac{\partial \ln g_{\text{HT}}(\sigma)}{\partial \eta}\right)
\]  
(6.18)

\[
Z^{\text{HSix}} = 2Z^{\text{HO}} - \left(1 + \eta \frac{\partial \ln g_{\text{HO}}(\sigma)}{\partial \eta}\right)
\]  
(6.19)

\[
Z^{32} = 2Z^{\text{HSix}} - \left(1 + \eta \frac{\partial \ln g_{\text{HSix}}(\sigma)}{\partial \eta}\right)
\]  
(6.20)

The equation of state for 32-mers can be solved as

\[
Z^{32} = 32Z^{\text{HS}} - 16 \left(1 + \eta \frac{\partial \ln g_{\text{HS}}(\sigma)}{\partial \eta}\right) - 8 \left(1 + \eta \frac{\partial \ln g_{\text{HD}}(\sigma)}{\partial \eta}\right) \\
- 4 \left(1 + \eta \frac{\partial \ln g_{\text{HT}}(\sigma)}{\partial \eta}\right) - 2 \left(1 + \eta \frac{\partial \ln g_{\text{HO}}(\sigma)}{\partial \eta}\right) \\
- \left(1 + \eta \frac{\partial \ln g_{\text{HSix}}(\sigma)}{\partial \eta}\right)
\]  
(6.21)

A general expression can be written as

\[
Z^m = mZ^{\text{HS}} - (m-1) - \eta \left\{ \frac{m}{2} \frac{\partial \ln g_{\text{HS}}(\sigma)}{\partial \eta} + \frac{m}{4} \frac{\partial \ln g_{\text{HD}}(\sigma)}{\partial \eta} \\
+ \frac{m}{8} \frac{\partial \ln g_{\text{HT}}(\sigma)}{\partial \eta} + \frac{m}{16} \frac{\partial \ln g_{\text{HO}}(\sigma)}{\partial \eta} + \frac{m}{32} \frac{\partial \ln g_{\text{HSix}}(\sigma)}{\partial \eta} \right\}
\]  
(6.22)

The equation of state for 4-, 8- and 16-mers can be written by taking into account the terms up to \(m/x = 1\). Equation (6.22) can be solved further for the two values of \(g(\sigma)\) proposed by Chiew [8]. The two values, \(g_1(\sigma)\) and \(g_2(\sigma)\), are as follows:
\[ g_1(\sigma) = \frac{2 + (3m - 2)\eta}{2m(1-\eta)^2}, \quad (6.23) \]

\[ g_2(\sigma) = \frac{(m+2) + (5m - 2)\eta}{4m(1-\eta)^2}. \quad (6.24) \]

Both the equations predict the same value of \( g(\sigma) \) for the disphere but different for higher m-mers. For \( g_1(\sigma) \), the equation of state can be solved as

\[
Z^m = mZ^H - (m-1) - \left( \frac{\eta}{1-\eta} \right) \left\{ \frac{m}{2} \left( \frac{5 - 2\eta}{2 - \eta} \right) + \frac{m}{4} \left( \frac{2 + \eta}{1 + 2\eta} \right) \right. \\
\left. + \frac{m}{8} \left( \frac{7 + 5\eta}{1 + 5\eta} \right) + \frac{m}{16} \left( \frac{13 + 11\eta}{1 + 11\eta} \right) + \frac{m}{32} \left( \frac{49 + 47\eta}{1 + 47\eta} \right) \right\} 
\]

(6.25)

For \( g_2(\sigma) \), the equation of state can be solved as

\[
Z^m = mZ^H - (m-1) - \left( \frac{\eta}{1-\eta} \right) \left\{ \frac{m}{2} \left( \frac{5 - 2\eta}{2 - \eta} \right) + \frac{m}{4} \left( \frac{2 + \eta}{1 + 2\eta} \right) \right. \\
\left. + \frac{m}{8} \left( \frac{5 + 3\eta}{1 + 3\eta} \right) + \frac{m}{16} \left( \frac{29 + 19\eta}{5 + 19\eta} \right) + \frac{m}{32} \left( \frac{113 + 79\eta}{17 + 79\eta} \right) \right\} 
\]

(6.26)

Recently, Chang and Sandler [16] have proposed the correlation function at contact for homonuclear hard sphere chain fluid using Wertheim integral equation theory as

\[
g(\sigma) = \frac{(1+\eta/2)^{\frac{1}{2}} - (m-1) \left( \frac{1}{(1-\eta)^\frac{1}{2}} - \frac{1}{m(1-\eta)} \right)}{(1-\eta)^\frac{1}{2}} \quad (6.27) \]
This gives the same expression for the contact value of \( g(\sigma) \) as given by \( g_1(\sigma) \) up to 16-mers. The last term for 32-mers in equation (6.25) is changed to \((25 + 23\eta)/(1 + 23\eta)\), however, the magnitude remains close to that obtained by equation (6.25). Thus, the equations of state obtained by using \( g(\sigma) \) proposed by Chang and Sandler predict the same values as those obtained by equation (6.25) up to 32-mers.

For comparison, we have also calculated the equation of state proposed by Ghonasgi and Chapman [7] derived by assuming

\[
\frac{\partial \ln g_{HT}(\sigma)}{\partial \eta} = \frac{\partial \ln g_{HD}(\sigma)}{\partial \eta} \text{ as}
\]

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

\[
x \left(1 + \frac{2\eta(2+n)}{(1-n)(1+2n)}\right)
\]

(6.28)

6.4 RESULTS AND DISCUSSION FOR HOMONUCLEAR HARD SPHERE TANGENT CHAIN MOLECULES

The equations of state predicted by the SAFT-D theory using equations (6.25) and (6.26) are compared with molecular simulation data [9-12] for homonuclear hard sphere chains of 8-mers and 16-mers in table 6.1. The values obtained using equation (6.28) are also shown in table 6.1. The compressibility factor for 4 mers will remain the same in all three cases, i.e., equations (6.25), (6.26) and (6.28). We find that equations (6.25) and (6.26)
provide better agreement with simulation data [9,12] in comparison with the values obtained by Ghonasgi and Chapman's equations state, i.e., equation (6.28). The data in table 6.1 indicate that equation (6.28) overpredicts the compressibility factor at all densities. This is due to the fact that an assumption \[(\ln g_{HO}(\sigma))/(\partial \eta) = (\partial \ln g_{HT}(\sigma))/(\partial \eta) = (\partial \ln g_{HD}(\sigma))/(\partial \eta)\] was made by them. Between equations (6.25) and (6.26), equation (6.26) seems to provide better results for higher mers, particularly, for 32-mers, as shown in table 6.2.

We have also compared our equation of SAFT-D system with other equations of state (discussed in Chapter-6 (6.2)) in table 6.3. We find that our equation of state presents better results and more close to simulation results than other equations of state.

We have discussed and presented the calculation of non-sphericity parameter \(\alpha\) for several other equations of state using different methods in Chapter-4. Here, we have presented the results of non-sphericity parameter \(\alpha\) using our equations of state in SAFT-D system (equation (6.25) and (6.26)) of tangent hard sphere chain fluids for 4-mers, 8-mers and 16-mers. We have applied here the same method of the calculations of \(\alpha\) as discussed in Chapter - 4 (4.2.3). As simulations results are not available for \(\alpha\), we can compare our results with those of other theoretical values such as GFD results presented in table 4.5.
Table - 6.1: Comparison of our equations of state of m hard sphere chain fluids with equation (6.28) and with simulation data [10-12].

\( \rho^* = m \rho \sigma^3 = 6\eta/\pi \).

<table>
<thead>
<tr>
<th></th>
<th>( Z^m )</th>
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<tbody>
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<td></td>
<td>8-mers</td>
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<tr>
<td>( \rho^* )</td>
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Table - 6.2: Comparison of equations of state of 32-mer hard sphere chain with molecular simulation as a function of reduced density \( \rho^* \).

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<th>( \rho^* )</th>
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206
Table - 6.3: Comparison of Molecular Simulation Data [9, 11, 12] with Equation of State Calculations for the Compressibility $D$ of m-Hard-Sphere Chains as a Function of Reduced Density ($\rho^* = m\rho^3$).

<table>
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<th>$\rho^*$</th>
<th>$m = 4$</th>
<th>$m = 8$</th>
<th>$m = 16$</th>
<th>$m = 32$</th>
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207
6.5 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 [17, 18]. The equation of state for FHS chains, however, is not as well developed as for tangent hard-sphere chains. This is because the TPT and the GF theories of tangent hard-sphere chain fluids can not be applied directly to FHS chain fluids, due to the lack of a well-defined reference monomer or dimer fluid.

Several attempts have been made to extend the TPT1 expressions to FHS chain fluids. One of the models is to relate the effective chain length to the scaled-particle-theory (SPT) parameter $\alpha$ at the second virial coefficient level [18–21]. This method yields an accurate equation of state but requires knowledge of the second virial coefficient [18, 20, 21]. Amos and Jackson [22] suggested replacing the FHS molecule with an "equivalent" tangent hard-sphere molecule, but the method is limited to small FHS molecules. Jackson and Gubbins [23] and Phan et al. [24] 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 [24].

While various methods have been used in extending TPT1 to FHS chain fluids, the extension of the GF theories to such fluids to focused 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 shorter 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 the 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 fraction is the same as that of the FHS chain fluid. Recently, Costa et al. [25] 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 provide more accurate predictions for the compressibility factors of the FHS chain fluids than either the GF or the GFD versions of approximation A or approximation B.

6.6 FORMULATION OF EFFECTIVE CHAIN LENGTH FOR FUSED HARD SPHERE CHAINS

Since the key to obtaining a TPT or GF equation of state rests on the choice of an appropriate reference system, we begin by considering various ways to define this reference system. The reference system for tangent hard-
sphere chains in the TPT and GF theories is formed by breaking the bonds between adjacent monomers along the tangent hard-sphere chains. However, for a homonuclear FHS chain of monomer diameter \( \sigma \) and bond length \( l \), such bond cleavage yields two types of

![Diagram of actual FHS chains and effective THS chains](image)

**FIG. 6.1**: Schematic representation of the shapes that result when a FHS chain model is broken into monomer. The effective tangent hard-sphere (THS) chain and the effective reference hard spheres are also shown. We assume that the effective THS chain fluid has the same compressibility factor as the FHS chain fluid.

oddly shaped particles (Fig. 6.1), for which there is no satisfactory theory. Since various methods can be used to approximate these oddly shaped particles, the reference system for FHS chain systems is not uniquely defined. Yet, it is generally agreed [16–25,19] that the volume fraction of the reference system, \( \eta^{\text{ref}} \), should be the same as the volume fraction of the FHS chain system, \( \eta^{\text{FHS}} \), i.e.,

\[
\eta^{\text{ref}} = \eta^{\text{FHS}} = \rho_{\text{ch}} V_{\text{ch}},
\]

(6.29)
Where $\rho_{\text{ch}}$ and $V_{\text{ch}}$ are the chain number density and the single chain volume, respectively. If we take a system of hard spheres as the reference system and imagine breaking each chain into $n_{\text{eff}}$ spheres with effective diameter $\sigma_{\text{eff}}$ (Fig. 6.1), we have

$$\frac{\pi}{6} n_{\text{eff}} \rho_{\text{ch}} (\sigma_{\text{eff}})^3 = \rho_{\text{ch}} V_{\text{ch}},$$

or

$$\frac{\pi}{6} n_{\text{eff}} (\sigma_{\text{eff}})^3 = V_{\text{ch}}.$$  \hspace{1cm} (6.31)

Here, the effective chain length of FHS chains, $n_{\text{eff}}$, can have a noninteger value, which is the consequence of overlap of adjacent monomers. The TPT1 equation of state for a system containing tangent hard-sphere chains of length $n_{\text{eff}}$ that are formed by the association of $n_{\text{eff}}$ hard-spheres (see Fig. 6.1) is given by [1, 2, 6]

$$\left[Z_{n_{\text{eff}}}^{\text{ex}} (\eta)\right]^{\text{THS}} = n_{\text{eff}} Z_1^{\text{ex}} (\eta) - (n_{\text{eff}} - 1) \eta \frac{d \ln g_1 (\eta)}{d \eta},$$

(6.32)

where $Z_1^{\text{ex}} (\eta)$ and $\left[Z_{n_{\text{eff}}}^{\text{ex}} (\eta)\right]^{\text{THS}}$ are the excess compressibility factors (over ideal) of the effective hard-sphere reference fluid and the effective THS chain fluid (which contains chains of length $n_{\text{eff}}$), respectively, $\eta$ is the volume fraction, and $g_1(\eta)$ is the contact value for the radial distribution function of the hard-sphere reference fluid. We now assume that the effective THS chain
fluid has the same compressibility factor as the FHS chain fluid that we are interested in. Thus the compressibility factor for FHS chains of length, \( n \), becomes

\[
[Z_n (l, \eta)]^{\text{FHS}} = 1 + \left[ Z_{n_{\text{eff}}}^{\text{ex}} (\eta) \right]^{\text{THS}} \\
= 1 + n_{\text{eff}} Z_{l}^{\text{ex}} (\eta) - (n_{\text{eff}} - 1) \eta \frac{d \ln g_1 (\eta)}{d \eta},
\]  

(6.33)

where the first term in eq. (6.33) is the ideal compressibility factor. Equation (6.33) is the same as the equations used in other TPT1 approaches for FHS chains. [18, 20, 21, 23, 24]. The question is how to obtain the effective chain length \( n_{\text{eff}} \), the only unknown in eq. (6.33). A clean way to do this is to choose \( n_{\text{eff}} \) so that the second virial coefficient predicted by eq. (6.33) is exact. [18, 20, 21] However, since the second virial coefficient is often unknown, we shall not explore this option further.

Before we try to find an expression for the effective chain length, \( n_{\text{eff}} \), it is often useful to examine the limits that \( n_{\text{eff}} \) satisfies. When the bond length \( l \rightarrow 0 \), the FHS chain reduces to a single hard sphere. As a result, we have the exact limit

\[
n_{\text{eff}} \rightarrow 1 \quad \text{as} \quad l \rightarrow 0.
\]  

(6.34)

In addition, the equation of state for the FHS chain fluid should reduce to the TPT1 equation of state for a THS chain fluid in the limit \( l \rightarrow 0 \). Therefore, we also have
\[ n_{\text{eff}} \to n \quad \text{as} \quad l \to \sigma. \quad (6.35) \]

A simple interpolation between these two limits will give us the expression used by Jackson and Gubbins [23]

\[ [n_{\text{eff}}]^{\text{JG}} = 1 + (n - 1) l^*. \quad (6.36) \]

or the expression used by Phan, Kierlik, and Rosinberg [24]

\[ [n_{\text{eff}}]^{\text{PKR}} = 1 + (n - 1) l^* \cdot l^* \cdot l^*. \quad (6.37) \]

where \( l^* \) is the reduced bond length \( = \frac{1}{\sigma} \). Although satisfying these two limits guarantees the accuracy of the FHS equation of state at \( l^* \sim 0 \) and \( l^* \sim 1 \), it does not guarantee the accuracy of the FHS equation of state for values in between. In fact, the FHS equation of state (6.33) using either eq. (6.36) or eq. (6.37) for the effective chain length, \( n_{\text{eff}} \), is inaccurate for \( l^* \sim 0.4 \) in comparison to the MC computer simulation results for 4-mer, 8-mer, and 16-mer FHS chains [25].

A more logical way of obtaining \( n_{\text{eff}} \) is to make use eq. (6.31). However, eq. (6.31) contains two unknowns (\( \sigma_{\text{eff}} \) and \( n_{\text{eff}} \)) in a single equation. Honnell and Hall [5] eliminated one of these unknowns by assuming that the effective hard sphere diameter, \( \sigma_{\text{eff}} \), is the same as the monomer diameter for the FHS chain, \( \sigma \). This assumption yields
\[ [n_{\text{eff}}]^A = \frac{6V_{\text{ch}}}{\pi \sigma^3}. \] (6.38)

This is called approximation A in order to be consistent with previous notation [17, 25]. It is easy to show that eq. (6.38) satisfies both eqs. (6.34) and (6.35). However, the resulting equation of state, called TPT1-A, is not very accurate. This is not surprising because one would expect that the effective reference monomer diameter, \( \sigma_{\text{eff}} \) must be different thus the monomer diameter \( \sigma \) in order to take into account the odd shape of the "actual" reference particles (Fig. 6.1). Yethiraj et al. [17] suggested an alternative approximation (approximation B) in which the effective chain-length is taken to be the same as the actual chain length, i.e.,

\[ [n_{\text{eff}}]^B = n. \] (6.39)

We shall not consider approximation B in this paper because it does not satisfy the exact limit, eq. (6.34). In order to obtain more accurate effective chain length, \( n_{\text{eff}} \), Costa et al. [25] supplemented eq. (6.31) with an additional equation that requires the surface area of the reference fluid to be the same as the surface area of the chain fluid. This equation is

\[ n_{\text{eff}} \pi (\sigma_{\text{eff}})^2 = S_{\text{ch}}. \] (6.40)

where \( S_{\text{ch}} \) is the surface area of the FHS chain. Equations (6.31) and (6.40) can be solved for the effective chain length \( n_{\text{eff}} \), to yield approximation AB
\[ [n_{\text{eff}}]^A_B = \frac{S_{ch}^3}{36\pi V_{ch}^2}. \] (6.41)

It is to show that eq. (6.41) satisfies both the \( l^* = 0 \) and \( l^* = 1 \) limits [Eqs. (6.34) and (6.35)].

If we use the accurate Carnahan–Starling equation of state to obtain the equation of state and the contact value of the radial distribution function for the hard-sphere reference fluid, [13] eq. (6.33) becomes

\[ Z_n(l,n) = 1 + n_{\text{eff}} \frac{2\eta(2-\eta)}{(1-\eta)^3} - (n_{\text{eff}} - 1) \frac{\eta(5-2\eta)}{(2-\eta)(1-\eta)} \] (6.42)

Thus the TPT1-A equation of state is eq. (6.42) with \( n_{\text{eff}} \) calculated form Eq. (6.38) while the TPT1-AB equation of state is eq. (6.42) with \( n_{\text{eff}} \) calculated from eq. (6.41).

For a rigid linear (straight) fused hard-sphere chain, the chain volume, \( V_{ch} \), and the chain surface area, \( S_{ch} \), satisfy

\[ V_{ch} = \frac{1}{6} \pi \sigma^3 \left\{ 1 + \frac{(n-1)}{2} l^* \right\} - 3 - (l^*)^2 \} \right\}, \] (6.43)

\[ S_{ch} = \pi \sigma^3 [1 + (n - 1)] l^* \] (6.44)

Equations (6.43) and (6.44) give

\[ [n_{\text{eff}}]^A = 1 + \frac{(n-1)}{2} l^* \right\} - 3 - (l^*)^2 \} \right\}, \] (6.45)
\[
[n_{\text{eff}}]_{AB}^{*p} = \frac{[1+(n-1)*]}{1+(n-1)1*\left[3-(1*)^2\right]/2}\]

We shall call eqs. (6.45) and (6.46) the straight chain approximation for the effective chain length. It is interesting to note that there is a relation between the effective chain length in approximation A and the effective chain lengths used by Jackson and Gubbins [23] and Phan et al. (24), give

\[
[n_{\text{eff}}]^A_c = \frac{3}{2}[n_{\text{eff}}]^G - \frac{1}{2}[n_{\text{eff}}]^P_K
\]

One more way is to adjust the number of beads per unit volume so that the reference monomer and dimer fluids have the same volume fraction and the same surface area as the fused hard-sphere chain fluid. Thus the effective number of monomers per unit chain, \(n_m\) and the monomer diameter \(d_m\), are adjusted so that

\[
n_m \frac{\pi d_m^3}{6} = \nu_n
\]

and

\[
n_m \pi d_m^2 = S_n
\]

i.e.

\[
d_m = \frac{6\nu_n}{S_n}
\]

the effective number of dimers per chain \(m^*\), the dimer diameter \(d\), are adjusted so that
\[ m^* \frac{\pi d^3}{6} \left[ 1 + \frac{3}{2\left( \frac{\ell}{d} \right)} - \frac{1}{2\left( \frac{\ell}{d} \right)^3} \right] = V_m \] (6.51)

and

\[ m^* \pi d^2 \left[ 1 + \left( \frac{\ell}{d} \right) \right] = S_m \] (6.52)

where \( S_m \) and \( V_m \) are the surface area and volume of a fused hard-sphere chain, respectively. We can obtain the value of \( m^* \) using equations (6.51) and (6.52) as

\[
m^* = \left( \frac{S_m^3}{36\pi V_m^2} \right) \left[ 1 + \frac{3}{2\left( \frac{\ell}{d} \right)} - \frac{1}{2\left( \frac{\ell}{d} \right)^3} \right]^2 \left[ 1 + \left( \frac{\ell}{d} \right)^3 \right]^{-3} \] (6.53)

6.7 RESULTS AND DISCUSSION OF EOS FOR FUSED HARD-SPHERE CHAIN MOLECULES

We have applied SAFT-D theory to fused hard-sphere chain molecules and we consider the equation (6.26) to describe the equation of state. To apply SAFT-D theory (eq. 6.26), the effective number of dimers per chain is taken as \( m^* \) described by equation (6.53) thus, by replacing \( m \) by \( m^* \) in equation (6.26), we can calculate the equation of state of the fused hard sphere chain of 4-mers, 8-mers and 16-mers at the reduced bond length \( l^* = (l/d) \), and for an effective volume fraction \( \eta \) varying from 0.05 to 0.45. The values of \( l^* \), \( S_m \), \( V_m \) and \( m^* \) are presented in table 6.5. We find that SAFT-D
theory adequately predicts the compressibility factor at all densities. The results are plotted in figure (6.2) 1 for 4-mers, 8-mers and are compared with the results of GFD theory [25] in the AB approximation and the simulation data [25]. Figure (6.2) reveals and SAFT-D theory (present work) underpredicts, and GFD theory overpredicts, the compressibility factor compared with simulation results. This discrepancy is almost negligible for 4 mers but increases with bond length. However, our results are closer to simulation results than those of GFD theory in the AB approximation for greater bond lengths, i.e., for 8-mers and 16-mers.

We have also compared our results obtained by m* with those of other approximations for effective chain length. Calculations are made using equation (6.41) and (6.46) for AB approximation of effective chain length applied in SAFT-D theory. The results are compared with Monte Carlo simulation results in table 6.7. We find that the values of effective chain length m* given by equation (6.53) describes better equations of state of Fused hard sphere chain molecules for m = 4, 8 and 16 mers than those of other effective chain length i.e., equations (6.41) and (6.46).

The non-sphericity parameter or shape factor α and virial coefficients have also been calculated by using the SAFT-D equation of state (equation (6.26) with (6.53). We observed the value of α is much reduced for fused hard sphere chain fluid in comparison to tangent hard-sphere chain fluid. The values of virial coefficients are also much reduced in comparison to the values of tangent hard sphere chain fluid. The values of all four virial
coefficients almost remain constant w.r.t. to $\eta$ for 4-mers. However, this variation of $B_2^*, B_3^*, B_4^*$, and $B_5^*$ w.r.t. $\eta$ increases for higher mers i.e., 8-mers and 16-mers.

**Table - 6.4:** The values of non-sphericity parameter $\alpha$ for Tangent hard-sphere chain molecules ($l^* = 1$) for $m = 4$, 8 and 16 using equation (25), (26) and (28) [$\rho^* = 6\eta/\pi$].

\[
\begin{array}{cccccccccc}
\hline
\rho^* & \text{Eq. (25)} & \text{Eq. (26)} & \text{Eq. (28)} & \text{Eq. (25)} & \text{Eq. (26)} & \text{Eq. (28)} & \text{Eq. (25)} & \text{Eq. (26)} & \text{Eq. (28)} \\
\hline
.1 & 1.98 & 1.96 & 1.94 & 2.62 & 2.96 & 3.08 & 3.29 & 5.04 & 5.38 \\
.2 & 2.19 & 2.19 & 2.13 & 3.34 & 3.54 & 3.65 & 5.29 & 6.12 & 6.58 \\
.3 & 238 & 2.39 & 2.30 & 3.93 & 4.05 & 4.13 & 6.82 & 7.33 & 7.64 \\
.4 & 256 & 2.52 & 2.46 & 4.44 & 4.51 & 4.58 & 8.07 & 8.40 & 8.62 \\
.5 & 2.72 & 2.72 & 2.63 & 4.88 & 4.94 & 4.98 & 9.13 & 9.35 & 9.51 \\
\hline
\end{array}
\]

**Table - 6.5:** Parameters used in the calculations of Fused hard sphere chain.

\[
\begin{array}{cccccc}
\hline
\text{Mers} & l/d & V_m & S_m & m^* & l^* \\
\hline
4 & 0.3664 & 1.422 & 6.905 & 1.311 & 0.4058 \\
8 & 0.3330 & 2.575 & 11.728 & 1.992 & 0.3948 \\
16 & 0.3195 & 4.920 & 21.547 & 3.404 & 0.3948 \\
\hline
\end{array}
\]
Table 6.6: Shape factor ($\alpha$) and virial coefficients of Fused hard-sphere chain fluids for $m = 4, 8$ and $16$ with the values of $l^*$ and $m^*$ given in table 6.5.

<table>
<thead>
<tr>
<th>$\eta$</th>
<th>$m$</th>
<th>$\alpha$</th>
<th>$B_2^*$</th>
<th>$B_3^*$</th>
<th>$B_4^*$</th>
<th>$B_5^*$</th>
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Table 6.7: Comparison of equations of state for different values of effective chain length, $[n_{eff}]^{AB}$ and $m^*$.

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221
Fig. 6.2: Compressibility factor versus volume fraction for 4-mers, 8-mers and 16-mers, our values (SAFT-D theory), solid line; GFD theory in AB approximation, dotted line; and MC simulation results, open circles.