CHAPTER 3

VARIOUS THEORIES FOR NON-HARD SPHERICAL MOLECULES

CONTENTS

3.1 SCALED PARTICLE THEORY (SPT)

3.2 BONDED HARD SPHERE (BHS) APPROACH

3.3 THEORY PROPOSED BY MAESO AND SOLANA FOR HCB FLUIDS
   3.3.1 Introduction
   3.3.2 Derivation of The Equation of State For Two Dimensional Hard Body Fluids
   3.3.3 Derivation of The Equation of State For Three Dimensional HCB Fluids
   3.3.4 Extension of Three Dimensional Hard Body Fluid to Fused Hard Spheres Fluids

3.4 RELATION OF NON-SPHERICITY PARAMETER WITH VIRIAL COEFFICIENTS
   3.4.1 Introduction
   3.4.2 Theory
   3.4.3 Derivation of Virial Coefficients
   3.4.4 Comparison of Approximate Virial Coefficients For Particles of Different Shapes
   3.4.5 Theoretical Predictions of Virial Coefficients of HLTs Models

3.5 INTEGRAL EQUATION THEORY
   3.5.1 Introduction
3.5.2 Polymer-Rism Theory
3.5.3 Chiew Model
3.5.4 Average Correlation Function g(r)
3.5.5 PY1 Approximation
3.5.6 PY2 Approximation

3.6 THERMODYNAMIC THEORY
3.6.1 Introduction
3.6.2 Pair Potential in TPT
3.6.3 Formulation of TPT
3.6.4 Chain Approximation
   (a) First Order TPT
   (b) Second Order TPT
   (c) Validity of TPT

3.7 EQUATIONS OF STATE FOR CHAIN MOLECULES
3.7.1 Flory and Flory-Huggins Theory
   (a) Introduction
   (b) Lattice Model
   (c) Extension to Off-Lattice Models
3.7.2 Generalized Flory Theory
3.7.3 Generalized Flory Dimer (GF-D) Theory

3.8 REFERENCES
3.1 **SCALED PARTICLE THEORY (SPT)**

Statistical mechanical description of fluids usually combine the Ornstein–Zernike (OZ) equation relating the direct and total correlation function and an appropriate closure relation, the Percus–Yevick (PY) and hypernetted chain (HNC) being the best known examples. Interestingly, the PY equation has an analytic solution for hard spheres [1, 2] and hard sphere mixtures [3] in odd dimensional spaces. A completely unrelated theoretical approach is the scaled particle theory (SPT) which is based on a consideration of the work required to insert an additional fluid particle into the system [4]. SPT yields analytic solution for the EOS in any dimension and remarkably, the SPT solution for bulk hard spheres is identical to that obtained with PY theory. The analytic solutions of SPT for two dimensional fluids are clearly of great interest in the context of adsorption studies. Another advantage of the SPT approach is that it is relatively easy to extend to treatment to general convex particle [5]. Although this is strictly a theory for convex molecules, SPT can be used to study the non-convex heteronuclear hard-dumbbell fluid by examining a system of equivalent convex molecules which just envelop the hard dumbbells. An expression for the compressibility factor of convex molecules was first given by Gibbons [6].

\[
Z^{\text{SPT}} = \frac{PV}{N_m KT} = \frac{1+(3\alpha^2+3\alpha-2)\eta+(1-3\alpha)\eta^2}{(1-\eta)^2}
\]  

(3.1)

as before \( \eta = \frac{\pi N_m (\sigma_1^3 + \sigma_2^3)}{6V} \) is the total packing fraction. In the context of
SPT, $\alpha$ is given by

$$\alpha = \frac{R_m S_m}{3 V_m} \quad (3.2)$$

where $R_m$ is the convex molecule's mean curvature integral divided by $4\pi$, $S_m$ is its hard surface area and $V_m$ its volume. For a heteronuclear hard-dumbbell molecule with hard sphere diameters $\sigma_1$ and $\sigma_2$, the mean curvature of the enveloping convex body and the surface area and volume of the molecule are given by

$$R_m = \frac{1}{4} \left( \sigma_1 + \sigma_2 + 1 + \frac{(\sigma_1 + \sigma_2)^2}{4I} \right) \quad (3.3)$$

$$S_m = \frac{\pi}{2} \left( \sigma_1^2 + \sigma_2^2 + 2\sigma_1 a + 2\sigma_2 b \right) \quad (3.4)$$

and

$$V_m = \frac{\pi}{12} \left( \sigma_1^3 + \sigma_2^3 + 3\sigma_1^2 a + 3\sigma_2^2 b - 4a^3 - 4b^3 \right) \quad (3.5)$$

Here $I = a + b$ is the sphere – sphere bond length, where $a$ and $b$ are the distances from the centers of spheres 1 and 2 to the intersecting plane. In the particular case of the systems with tangent spheres, $I = (\sigma_1 + \sigma_2)/2$, $a = \sigma_1/2$, and $b = \sigma_2/2$.

In order to obtain the correct hard – sphere limit, Boublik [7] modified (3.1) into an equation of state of the form
which is referred to as the improved scaled particle theory (ISPT).

When the molecules are spherical, \( \alpha = 1 \) and (3.6) reduces to the Carnahan and Starling expression given by

\[
Z_{CS}^{\text{CS}} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}
\]  

(3.7)

where \( \eta = \pi \sigma_i^3 N_i / (6V) \) is the total packing fraction and \( N_i \) is the number of spheres. It gives a good representation of the properties of molecules which are moderately non-spherical.

More recently, Boublik and coworkers [8, 9] have used the relationships obtained for associating spherical molecules [10, 11] to obtain a linear dependence of the virial coefficients on the non-sphericity parameter \( \alpha \). The expression for the second virial coefficient has also been reported in a later study by Walsh and Gubbins [12]. By keeping to the Carnahan and Starling form for the compressibility factor in such a way that the relationships obtained with the associating fluid approach are retained, the following equation is obtained [8].

\[
Z_{SPI}^{\text{SPI}} = \frac{1}{(1 - \eta)} + \frac{3\alpha \eta}{(1 - \eta)^2} + \frac{\eta^2 \left[ 49\alpha - 31 - \eta(11\alpha - 7) - \eta^2(25\alpha - 21) \right]}{6(1 - \eta)^3}
\]  

(3.8)

The above equation with \( \alpha \) given by equation (3.2) can be used as the
equation of state for the heteronuclear hard-dumbbell system. Equation (3.8) has been shown to be a good representation of the properties of a variety of fused hard-sphere, FHS model systems including homonuclear and heteronuclear diatomics, linear and bent tri-atomics, and tertatomics [8-12].

The problem with any scaled particle theory arises in the determination of the parameter $\alpha$. A numerical method is usually employed for large polyatomic FHS molecules [12,13] but in the case of linear molecules this is not necessary since analytical expressions can be obtained for $R_m$, $S_m$ and $V_m$.

For FHS triatomic molecules with a 1–2 bond length of $l_{12} = a + b$, the distances from the centres of spheres 1 and 2 to the intersecting plane of the two spheres are $a$ and $b$, where

$$a = \frac{1}{2} \left[ l_{12} + \frac{\sigma_1^2 - \sigma_2^2}{4l_{12}} \right]. \quad (3.9)$$

Similarly, the 2–3 bond length is $l_{23} = c + d$, the distances from the centres of spheres 2 and 3 to the intersecting plane of the two spheres are $c$ and $d$, and

$$d = \frac{1}{2} \left[ l_{23} + \frac{\sigma_3^2 - \sigma_2^2}{4l_{23}} \right]. \quad (3.10)$$

The other distances $b$ and $c$ are given in terms of the bond lengths by $b = l_{12} - a$ and $c = l_{23} - d$. Note that for BHS molecules with tangentially fused hard spheres
\[ a = \sigma_1/2, \ b = c = \sigma_2/2, \ d = \sigma_3/2, \ l_{12} = (\sigma_1 + \sigma_2)/2 \text{ and } l_{23} = (\sigma_2 + \sigma_3)/2. \]

The molecular surface area and volume of linear FHS triatomics are given by

\[ S_m = \frac{\pi}{2} \left( \sigma_1^2 + \sigma_3^2 + 2a\sigma_1 + 2(b+c)\sigma_2 + 3d\sigma_3 \right) \]  \hspace{1cm} (3.11)

and

\[ V_m = \frac{\pi}{2} \left( \sigma_1^3 + \sigma_3^3 + 3a\sigma_1^2 + 3(b+c)\sigma_2^2 + 3d\sigma_3^2 - 4(a^3 + b^3 + c^3 + d^3) \right)  \]  \hspace{1cm} (3.12)

Analytical expressions for \( S_m \) and \( V_m \) of FHS triatomics have been given by Lustig [14] for a range of molecular geometries, but no results are presented for the mean curvature integral \( R_m \).

The mean-curvature integral is difficult to evaluate for the convex bodies of nonlinear FHS molecules. But it is analytical in the case of linear systems. For symmetrical triatomic molecules with \( \sigma_1 = \sigma_3 \leq \sigma_2 \) and \( l_{12} = l_{23} \), the mean-curvature integral is [15].

\[ R_m = \frac{1}{4} \left[ 2\sigma_1 + 2l_{12} + \frac{(\sigma_2 - \sigma_1)^2}{2l_{12}} \right], \]  \hspace{1cm} (3.13)

The equivalent convex body has the shape of a diamond with rounded edges. When the end spheres become larger than the central sphere with \( \sigma_1 = \sigma_3 \geq \sigma_2 \), the convex body is a prelate spherocylinder with
\[ R_m = \frac{1}{2}(\sigma_1 + l_{12}) \]  

(3.14)

In general, the mean–curvature integral for the convex body of a linear asymmetrical FHS triatomic with \( \sigma_1 \neq \sigma_2 \neq \sigma_3 \) and \( \sigma_3 \leq [\sigma_2 (l_{12} + l_{23}) - \sigma_1 l_{23}] / l_{12} \) is [16].

\[
R_m = \frac{1}{4\pi} \left[ \int_0^{2\pi} \int_0^\pi \frac{d\phi}{sin \theta} \frac{d\theta}{sin \theta} \right] H(\phi, \theta) \sin \theta \\
= \frac{1}{2} \int_0^{\pi} \frac{d\theta}{sin \theta} \sin \theta \\
= \frac{1}{4} \left[ \sigma_1 + \sigma_3 + l_{12} + l_{23} + \frac{(\sigma_2 - \sigma_1)^2}{4l_{12}} + \frac{(\sigma_2 - \sigma_3)^2}{4l_{23}} \right],
\]

(3.15)

Here, the perpendicular distance from an arbitrary molecular origin to the supporting plane in the direction \( \theta, H(\theta) \), is independent of \( \phi \). The size of sphere 3 relative to spheres 1 and 2 ensures that the resulting convex body does not engulf sphere 2. When \( \sigma_3 \geq [\sigma_2 (l_{12} + l_{23}) - \sigma_1 l_{23}] / l_{12} \), \( R_m \) is given by

\[
R_m = \frac{1}{4} \left[ \sigma_1 + \sigma_3 + l_{12} + l_{23} + \frac{(\sigma_1 - \sigma_3)^2}{4(l_{12} + l_{13})} \right],
\]

(3.16)

For this system, sphere 2 is included within a convex body shaped like drop.

The above expressions for the mean–curvature integrals, surface area and volume of the linear FHS triatomic molecules can be used to calculate the parameter of nonsphericity using (3.2). Once \( \alpha \) is known (3.6), and (3.8) can be used as the equations of state for the FHS triatomic molecules. The
adequacy of the SPT equations of state (3.6) and (3.8) in describing the properties of linear symmetrical and asymmetrical heteronuclear triatomics of tangent hard spheres is determined by comparison with exact Monte Carlo simulation data.

\[ l = \frac{(\sigma_1 + \sigma_2)}{2}. \]

Fig 3.1: The heteronuclear hard dumbbells consist of two tangent hard spheres of diameters \( \sigma_1 \) and \( \sigma_2 \) with a center–to–center distance of \( l = \frac{(\sigma_1 + \sigma_2)}{2} \).

3.2 BONDED HARD–SPHERE (BHS) APPROACH

The model diatomic molecules of interest are formed by fusing together two hard spheres of diameters \( \sigma_1 \) and \( \sigma_2 \) so that the center–to–center distance is \( l = \frac{(\sigma_1 + \sigma_2)}{2} \) (see fig. 3.1). Our starting point for a theory of these heteronuclear hard dumbbells is an equimolar binary mixture of the constituent monomer hard spheres. An accurate equation of state for multicomponent hard-sphere mixtures has been given by Mansoori et al. [17, 18]. The compressibility factor of a binary mixture of hard spheres with diameters \( \sigma_1 \) and \( \sigma_2 \) is given by
\[ \frac{Z^{\text{hs}}}{NkT} = \frac{PV}{\pi \rho} \left( \frac{\xi_0}{1 - \xi_3} + \frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{3\xi_2^3}{(1-\xi_3)^3} + \frac{\xi_3^3}{(1-\xi_3)^3} \right), \]  

(3.17)

Where \( P \) is the pressure of the system, \( V \) the volume \( N = N_1 + N_2 \) the number of spheres, \( T \) the temperature, \( \rho = N/V \) the total number density, and \( k \) Boltzmann's constant. The reduced densities \( \xi_i \) are defined as

\[ \xi_i = \frac{\pi \rho}{6} \left( x_1 (\sigma_1)^i + x_2 (\sigma_2)^i \right) \]  

(3.18)

For equimolar mixtures the mole fractions of the two components are equal, \( x_1 = N_1/N = x_2 = N_2/N = \frac{1}{2} \), which simplifies the equations.

Anisotropic bonding sites are then placed on the hard spheres of components 1 and 2 to allow for 1–2 dimerization. The bonding site represents a strong and short-range attractive interaction such as an off-center square–well potential. The precise nature of the site need not, however, be specified in the following discussion. By restricting the association to dimer formation, the system will consist of monomer and dimer species in equilibrium for finite values of the site-site interaction energy. The position of the monomer–dimer equilibrium can be controlled by varying the strength of this bonding interaction. In the limit of complete bonding corresponding to infinite values of the site-site interaction energy, all spheres of component 1 are bonded to spheres of component 2.
Heteronuclear Hard Dumbbells

Fig. 3.2: The diatomic molecules are formed by bonding together two components of a binary hard-sphere mixture with association sites. The monomer–dimer equilibrium can be shifted to the right by increasing the strength of the site-site interaction.

Forming a system of pure heteronuclear hard-dumbbell molecules (see fig. 3.2) Hence, if the thermodynamic properties of the associating hard-sphere mixture are known, those of the corresponding heteronuclear hard-dumbell system can be obtained in the limit of complete association.

The properties of a multicomponent hard-sphere mixture with multiple bonding sites can be solved in the context of a relatively simple thermodynamic perturbation theory [10, 19] and an equation of state for the dimerizing binary hard-sphere mixture in question can be obtained as a special case of the general expressions. This type of theory was first used by Wertheim to deal with pure molecules with one attractive site [20, 21] and it was later extended to systems with multiple sites [22, 23]. Extensive comparisons with computer simulation data have shown that the theory accurately describes the properties of these types of associating molecules [24, 25, 11].

The compressibility factor of an associating binary hard-sphere mixture can be written in the form
\[ Z^{\text{mix}} = \frac{PV}{NkT} = Z^{\text{hs}} + Z^{\text{bond}} \]  

(3.19)

This is basically the hard-sphere reference term \( Z^{\text{hs}} \) with a perturbation term \( Z^{\text{bond}} \) which includes the contributions due to bonding. In the case of a system with single bonding sites. A on component 1 and B on component 2 so that only 1-2 dimerization is possible. \( Z^{\text{bond}} \) is given by [10, 19].

\[ Z^{\text{bond}} = \rho x_1 \left( \frac{\partial x_a}{\partial \rho} \right)_{T,N} \left( \frac{1}{x_A} - \frac{1}{2} \right) + \rho x_2 \left( \frac{\partial x_b}{\partial \rho} \right)_{T,N} \left( \frac{1}{x_B} - \frac{1}{2} \right). \]  

(3.20)

This bonding contribution is written in terms of \( X_A \) and \( X_B \) which are the fractions of components 1 and 2 not bonded at sites A and B. and in terms of their density derivatives. Following the approach of Wertheim, \( X_A \) and \( X_B \) are obtained from

\[ X_A = \frac{1}{1 + \rho x_2 x_B \Delta}, \]  

(3.21)

and

\[ X_B = \frac{1}{1 + \rho x_1 x_A \Delta}, \]  

(3.22)

Since the number of molecules of component 1 bonded at A, \( X_1 N (1 - X_A) \), must equal the number of molecules of component 2 bonded at B, \( X_2 N (1 - X_B) \), \( X_B \) can be given in terms of \( X_A \) as
\[ X_B = 1 - \frac{X_1}{XX_2} (1 - X_A) \]  \hspace{1cm} (3.23)

For the equimolar mixture of interest \( X_1 = X_2 = 1/2 \) and \( X_A = X_B \), so that the contributions due to bonding at sites A and B are equivalent. Hence, the bonding term given by (3.20) becomes

\[ Z_{\text{bord}} = \rho \left( \frac{\partial X_A}{\partial \rho} \right)_B \left( \frac{1}{X_A} - \frac{1}{2} \right) \]  \hspace{1cm} (3.24)

and \( X_A \) is obtained from the quadratic equation

\[ \left( \frac{\rho \Delta_{AB}}{2} \right) X_A^2 + X_A - 1 = 0. \]  \hspace{1cm} (3.25)

The function \( \Delta_{AB} \) depends on the structure of the hard-sphere reference mixture and on the strength and range of the bonding interaction. A good approximation for \( \Delta_{AB} \) in the case of short-range site-site interactions is [10, 11].

\[ \Delta_{AB} = 4 \pi g_{12}^{hs}(\sigma_{12}) \sigma_{12}^2 \int < f_{AB}(12) > \omega_1 \omega_2 dr_{12}. \]  \hspace{1cm} (3.26)

The term \( g_{12}^{hs}(\sigma_{12}) \) is the contact value of the 1-2 sphere-sphere distribution function for the reference hard-sphere mixture where \( \sigma_{12} = (\sigma_1 + \sigma_2)/2 \); this separation also represents the bond length \( l \) of the heteronuclear hard dumbbells \( < f_{AB}(12) > \omega_1 \omega_2 = < \exp\left( - \frac{\phi_{bord}}{kT} \right) > - 1 > \omega_1 \omega_2 \) represents an angle average of the Mayer \( f \) function over all orientations of spheres 1 and 2.
The integral of (3.26) is over the intermolecular separation \( r_{12} \). In the following approach, the particular choice of the anisotropic site-site intermolecular potential \( \phi_{AB}^{\text{bond}} \) is unimportant. It is clear from the above equations that a knowledge of the pair distribution function at contact provides a route to the thermodynamic properties of the associating system.

The association has to be taken to completion for the fully-bonded heteronuclear hard-dumbbell system to be formed. This can be achieved if the strength of the bonding interaction tends to infinity as its range tends to zero so that the bonding potential is infinite only at hard-sphere contact. A similar approach has been used \([26]\) previously for homonuclear hard dumbbells and chains of hard spheres in \([10]\) the limit of total bonding the fractions of molecules not bonded at sites A and B are zero, \( X_A = X_B = 0 \), and (3.25) can be written

\[
\lim_{X_A \to 0} \left[ \left( \frac{\rho \Delta_{AB}}{2} \right) X_A^2 + X_A - 1 \right] = \left( \frac{\rho \Delta_{AB}}{2} \right) X_A^2 - 1 = 0
\]  

(3.27)

and rearranged to give

\[
X_A^2 = \frac{2}{\rho \Delta_{AB}}
\]  

(3.28)

The compressibility factor is obtained from (3.24) by differentiating (3.25) with respect to number density. After some algebra we find that
\[ Z_{\text{bord}} = -\frac{\rho x_A^2}{4} \left[ \Delta_{AB} + \rho \left( \frac{\partial \Delta_{AB}}{\partial \rho} \right)_{T,N} \right]. \quad (3.29) \]

In the limit of complete bonding (3.28) can be used (3.29) to give

\[ \lim_{x_A \to 0} Z_{\text{bord}} = -\frac{1}{2} \left[ 1 + \frac{\rho}{\Delta_{AB}} \left( \frac{\partial \Delta_{AB}}{\partial \rho} \right)_{T,N} \right]. \quad (3.30) \]

Since the limiting value of the integral in the definition of \( \Delta_{AB} \) (3.26) is equal to \( g^{hs}_{12}(\sigma_{12}) \) but for a multiplying constant, (3.30) can be written in terms of the contact value of the hard-sphere pair distribution function:

\[ \lim_{x_A \to 0} Z_{\text{bord}} = -\frac{1}{2} \left[ 1 + \frac{\rho}{g^{hs}_{12}(\sigma_{12})} \left( \frac{\partial g^{hs}_{12}(\sigma_{12})}{\partial \rho} \right)_{T,N} \right]. \quad (3.31) \]

\( g^{hs}_{12}(\sigma_{12}) \) is accurately given by [25,14]

\[ g^{hs}_{12}(\sigma_{12}) = \frac{1}{(1 - \xi_3)^3} + 3 \left( \frac{\sigma_1 \sigma_2}{\sigma_1 + \sigma_2} \right) \frac{\xi_2}{(1 - \xi_3)^2} + 2 \left( \frac{\sigma_1 \sigma_2}{\sigma_1 + \sigma_2} \right)^2 \frac{\xi_2^2}{(1 - \xi_3)^3}, \quad (3.32) \]

and the derivative of \( g^{hs}_{12}(\sigma_{12}) \) with respect to the density of spheres is

\[ \rho \left( \frac{\partial g^{hs}_{12}(\sigma_{12})}{\partial \rho} \right)_{T,N} = \frac{\xi_3}{(1 - \xi_3)^2} + 3 \left( \frac{\sigma_1 \sigma_2}{\sigma_1 + \sigma_2} \right) \frac{\xi_2}{(1 - \xi_3)^2} \frac{\xi_3(1 + \xi_3)}{(1 - \xi_3)^3}, \]

\[ + 2 \left( \frac{\sigma_1 \sigma_2}{\sigma_1 + \sigma_2} \right)^2 \frac{\xi_2^2}{(1 - \xi_3)^4} (2 + \xi_3) \quad (3.33) \]

The last stage in obtaining an equation of state for the heteronuclear
hard-dumbbells is to combine the hard-sphere and bonding contributions in (3.19). The compressibility factor for the system is given by

\[
Z_{\text{hthd}} = \frac{PV}{N_m kT} = 2 \left( Z_{\text{hs}}^{\text{lim}} + x_A \lim_{x_A \to 0} Z_{\text{bond}} \right).
\] (3.34)

The factor of 2 is included because the compressibility factor is given in terms of the number of molecules \(N_m\) not the number of hard spheres \(N\). Finally, combining the terms (3.17) and (3.34) we have

\[
Z_{\text{hthd}} = 12 \left[ \frac{\xi_0}{1 - \xi_3} + \frac{3\xi_1\xi_2}{(1 - \xi_3)^2} + \frac{3\xi_2^3}{(1 - \xi_3)^3} - \frac{\xi_3^3}{(1 - \xi_3)^3} \right]
\]

\[
- \left[ 1 + \frac{\rho}{\rho_{\text{hs}}^{\text{lim}}(\xi_1)} \left( \frac{\partial Z_{\text{bond}}}{\partial \rho} \right)_{T,N} \right],
\] (3.35)

The total packing fraction of the system is given by

\[
\eta = \xi_3 = \pi (\sigma_1^3 + \sigma_2^3) N_m / (6V)
\]

In the limiting case where \(\sigma_2 = 0\), the diameter ratio \(R = \sigma_2 / \sigma_1 = 0\) and (3.35) reduces to the Carnahan and Starling equation for pure hard spheres:

\[
Z_{\text{cs}} = \frac{PV}{N_1 kT} = \frac{1 + \eta + \eta^2 + \eta^3}{(1 - \eta)^3},
\] (3.36)

where \(\eta = \pi \sigma_1^3 N_1 / (6V)\) is the total packing fraction and \(N_1\) is the number of spheres of type 1. When the spheres are the same size \(\sigma_1 = \sigma_2 = \sigma_3\), the diameter ratio \(R = 1\) and the equation becomes that of the homonuclear hard-
dumbbell system [26, 10]:

\[
Z^{hp} = \frac{PV}{N_m kT} = 2 \left( \frac{1 + \eta + \eta^2 + \eta^3}{(1-\eta)^3} \right) - \frac{1 + \eta - \eta^2/2}{(1-\eta)(1-\eta/2)'}
\]

(3.37)

Where the packing fraction is now \( \eta = \pi \sigma^3 N/(6V) \).

3.3 **THEORY PROPOSED BY MAESO AND SOLANA FOR HCB FLUIDS**

3.3.1 **Introduction**

Maeso and Solana [27-30] proposed a simple and accurate equation of state for fluids of hard convex bodies from the pressure equation. The model relates the equation of state of two dimensional and three dimensional linear hard body fluids to the hard disk fluid and hard sphere fluid respectively. They have derived theoretically an equation of state for hard convex fluids (HCB) without making use of virial coefficients or any kinds of fitting parameters. In obtaining equation of state they have introduced some approximations where reliability was tested by analysing simulation data. The model requires the knowledge of the geometrical characteristic of the molecules. The word was started from two and three dimensional Homonuclear hard convex bodies and were later extended the hetero-nuclear hard dumbbells and fluid mixture of Homonuclear hard dumbbells in two dimensional and three dimensional bodies. They further extended their work to two dimensional hard cyclic n-mer fluids. Their results reproduce simulation data with in the uncertainly for all the molecules geometrically considered.
3.3.2 Derivation of the Equation of State for Two Dimensional Hard-body Fluids

Consider a pair of two-dimensional hard convex molecules in contact and reference point within each defining a position vector \( r_{12} \). Consider also the following quantities averaged over all possible relative orientations of the pair of molecules: \( g^{av}(0) \) the averaged contact value of the pair correlation function; \( \sigma^{av} = \langle r_{12} \cdot \mathbf{u} \rangle \), where angular brackets denote the average and \( \mathbf{u} \) is the unit vector normal to the surface at the contact point; and \( S_{1+2} \), the perimeter of the body formed by the reference point molecule 2 when this molecule moves around molecule 1 with the two molecules remaining in contact. We are interested in single component systems, for which \( S_{1+2} = 2S \), where \( S \) is the perimeter of a molecule. Then, from the virial theorem, the compressibility factor for a two-dimensional HCB fluid, which occupies surface \( A \), and has a number density \( \rho = N/A \) is expressed in the form \([31, 32]\).

\[
Z^{HCB} = \frac{PA}{NkT} = 1 + \frac{1}{4} \rho 2S \sigma^{av} g^{av}(0)
\]  
(3.38)

Alternatively, taking into account that the mean radius of curvature of the molecule is \( R = S/2\pi \), we can put \( S_{1+2} = S + 2\pi R \), and

\[
Z^{HCB} = \frac{PA}{NkT} = 1 + \frac{1}{4} \rho (S + 2\pi R) \sigma^{av} g^{av}(0)
\]  
(3.39)

For a system of hard disks with diameter \( \sigma^{HD} \), expression (3.38) with
\[ \sigma^v = \sigma^{\text{HD}}, \quad g^v(0) = g^{\text{HD}}(0), \quad \text{and} \quad S = \pi \sigma^{\text{HD}}, \] reduces to

\[ Z^{\text{HD}} = 1 + \frac{1}{2} \pi \rho \left( \sigma^{\text{HD}} \right)^2 g^{\text{HD}}(0) \]  \hspace{1cm} (3.40)

So that, for the same density \( \rho \):

\[ \frac{Z^{\text{HCB}} - 1}{Z^{\text{HD}} - 1} = \frac{(S + 2\pi R) \sigma^{av} g^{av}(0)}{2\pi (\sigma^{\text{HD}})^2 g^{\text{HD}}(0)}. \]  \hspace{1cm} (3.41)

Defining the shape factor as

\[ \alpha = \frac{S^2}{2\pi A_m}, \]  \hspace{1cm} (3.42)

Where \( A_m \) is the area of a molecule, and considering disks with area

\[ A_m = \left( \frac{1}{4} \right) \pi \left( \sigma^{\text{HD}} \right)^2 \]
equal to that of the HCB molecule, we can transform

expression (3.41) into

\[ \frac{Z^{\text{HCB}} - 1}{Z^{\text{HD}} - 1} = \frac{1}{8} \left( \frac{2\pi \alpha}{S} + \frac{2\pi R}{A_m} \right) \sigma^{av} g^{av}(0). \]  \hspace{1cm} (3.43)

which can be put in the form

\[ \frac{Z^{\text{HCB}} - 1}{Z^{\text{HD}} - 1} = \frac{1}{2} \left( \frac{\alpha + \pi R^2}{2} \right) \frac{\sigma^{\text{HD}}}{A_m} \left( \frac{\sigma^{av} g^{av}(0)}{g^{\text{HD}}(0)} \right). \]  \hspace{1cm} (3.44)

For hard disks, an accurate equation of state has been obtained in the form [33].
\[ Z^{HD} = \frac{1 + y^2 / 8}{(1 - y)^2}, \]  

(3.45)

where \( y = \rho A_m \) is the packing fraction. From this expression we can also obtain \( g^{HD}(0) \). However, we still need to determine \( \sigma^{av} \) and \( g^{av}(0) \).

From the simulation data [32] for discorrections (HRD) (two-dimensional hard sphero-cylinders) with maximum length to breadth ratio \( k = 3 \), \( \sigma^{av} \) slightly decreases as density increases. Therefore, we can consider the ratio \( \sigma^{av}/\sigma^{HD} \), where \( \sigma^{HD} \) is the diameter of a disk with the same area as the discorrection, to roughly constant with moderate mean value which, in the range of densities, is 0.97, \( g^{av}(0) \) varies much more markedly, increasing with density, as is to be expected. However, with \( g^{HD}(0) \) determined from equation (3.45) for the same packing fractions, the ratio \( \sigma^{av}/\sigma^{HD}(0) \) is nearly a constant, whose value is 1.05 on average for the range of densities considered. As a consequence, we see that ratio \( \sigma^{av} g^{av}(0)/\sigma^{HD} g^{HD}(0) \) is nearly independent of density and has a mean value of 1.02. Thus at least for HDR with \( k = 3 \) and for moderate to high densities, as a good approach.

\[ \frac{\sigma^{av} g^{av}(0)}{\sigma^{HD} g^{HD}(0)} \approx 1. \]  

(3.46)

3.3.3 Derivation of the Equation of State for Three Dimensional HCB Fluids

The compressibility factor of an HCB fluid can be expressed [34]
\[ Z^{\text{HCB}} = 1 + \frac{1}{6} \rho S_{1+2} \sigma^{av} g^{av}(0), \quad (3.47) \]

Where \( g^{av}(0) \) is the contact value of the pair correlation function averaged over all orientations of the pair of molecules 1 and 2, \( \sigma^{av} = \langle r_{12} \rangle \) with \( r_{12} \) the position vector from a reference point in molecule 1 to another in molecule 2, and \( \nu \) the unit vector normal to the surface at the contact point. \( S_{1+2} \) is the surface area of a body defined by the center of molecule 2 moving around molecule 1 while the two molecules remain in contact for equal molecules.

\[ S_{1+2} = 2S + 8\pi \nu^2, \quad (3.48) \]

where \( S \) is the surface of the molecule and \( R \) its mean radius of curvature. For hard spheres of diameter \( \sigma \), expression (2.47) transforms into

\[ Z^{\text{HS}} = 1 + \frac{1}{6} \rho \sigma g^{\text{HS}}(0) 4\pi \sigma^2 = 1 + \frac{2}{3} \pi \sigma^3 g^{\text{HS}}(0), \quad (3.49) \]

So that for a given density \( \rho \)

\[ \frac{Z^{\text{HCB}} - 1}{Z^{\text{HS}} - 1} = 3 \left( S + 4\pi R^2 \right) \rho \sigma^{av} g^{av}(0) \left( \frac{2}{3} \pi \sigma^3 g^{\text{HS}}(0) \right). \quad (3.50) \]

If we consider spheres with volume \( v_m = (\pi/6) \sigma^3 \) equal to that of the HCB molecules, the packing fraction \( y = \rho v_m \) will be the same and
\[
\frac{Z^{HCB} - 1}{Z^{HS} - 1} = \left( S + 4\pi R^2 \right) \frac{g^{av}_{HS}(0)}{12\nu_m g^{av}_{HS}(0)}.
\]

(3.51)

or, in terms of the shape factor \( \alpha = RS/3\nu_m \)

\[
\frac{Z^{HCB} - 1}{Z^{HS} - 1} = \frac{1}{2} \left( \alpha + \frac{4\pi R^3}{\nu_m} \right) \frac{\sigma^{av}_{HS} g^{av}_{HS}(0)}{2R g^{HS}_{HS}(0)}.
\]

(3.52)

The right-hand side of expression (3.52) depends on the shape of the molecule. It also depends slightly on density through the density dependency of both \( g^{av}_{HS}(0) \) and \( \sigma^{av} \), especially the former, as revealed by the simulation data for hard oblate spherocylinders [35] with maximum diameter to thickness ratios \( \gamma = 2.0 \) and 3.0. However, this table also shows that the ratio \( \sigma^{av} g^{av}(0)/2R g^{HS}(0) \), with \( g^{HS}(0) \) determined from the CS equation [36] and \( R \) from geometry, varies only slightly with density and is very close to unity. Hence, at least for oblate spherocylinders with these values of \( \gamma \), we can write

\[
\frac{\sigma^{av}_{HS} g^{av}_{HS}(0)}{2R g^{HS}(0)} \approx 1.
\]

(3.53)

and thus

\[
\frac{Z^{HCB} - 1}{Z^{HS} - 1} \approx \frac{1}{2} \left( \alpha + \frac{4\pi R^3}{\nu_m} \right).
\]

(3.54)
which depends on the shape of the molecule, but not on density.

Note that for a sphere $4\pi R^2 = RS$ and $\sigma^v = \sigma = 2R$. For HCB with shapes not different very much from Spherecity, that is, for values of the shape factor $\alpha$ close to 1, we can approximate $4/3\pi R^3/v_m = RS/3$ $v_m = \alpha$ and thus, from expression (3.54)

$$\frac{1}{2} \left( \alpha + \frac{\left( \frac{4}{3} \right) \pi R^3}{v_m} \right) \approx \alpha$$

(3.55)

and

$$Z^{HCB} = 1 + \alpha(Z^{HS} - 1)$$

(3.56)

This equation resembles the hard chain equation of state used for the reference fluid in the perturbed hard chain theory for real fluids [37, 38] by replacing $Z^{HS}$ with a compressibility factor derived either from CS or from the strobridge equation of state. The shape factor $\alpha$ and the molecular volume $v_m$ were treated as fitting parameter.

3.3.4 Extension of Three Dimensional Hard Body Fluid to Fused Hard Spheres Fluids

The same formalism used to derive expression (3.56) has been shown to apply also to linear fused hard sphere fluids [30]. However, when the equation of the form (3.56) is tested for fused hard sphere fluids, the values of
the ratio \( \left( Z^{\text{sim}} - 1 \right) / \left( Z^{\text{CS}} - 1 \right) \) show an appreciable increase with packing fraction \( y \), especially for large values of the center-to-center distance \( l \). This is because fused hard spheres are not convex molecules, and thus, the inaccessible volume, which determines the pressure, is greater than the molecular volume [39] as shown in figure 3.3. Consequently, we must consider this "effective molecular volume" \( V_m^{\text{ef}} \) instead of \( V_m \), and the corresponding effective packing fraction would be \( y_{\text{ef}} = \rho V_m^{\text{ef}} \).

![Diagram](image)

**Fig. 3.3:** Shaded area shows the difference between effective volume and real volume for homonuclear dumbbells.

An expression for the effective molecular volume of an \( n \)-site linear body has been derived [39] in the form:

\[
v_n = (n-1) v_{ss} + \frac{\pi \sigma^3}{6} = \frac{\pi \sigma^3}{6} \left[ 1 + 3L - \frac{L^3}{2(n-1)^2} - 3(n-1)h \theta \right],
\]

(3.57)
where

\[ \nu_{ss} \left( \frac{\pi \sigma^3}{6} \right) \left( 3l - 1 \frac{3}{2} - 3h \theta \right) \]

(3.58)

is the volume between two consecutive sites separated by a distance \( l \), \( L = (n-1)l \), \( h = (1 - l^2/4)^{1/2} \) and \( \theta = \sin^{-1}(1/2) \), all the distances expressed in terms of the diameter \( \sigma \) of the spheres.

Using expression (3.57) for \( \nu_m^e \), and the corresponding values of \( y_{ef} \), in C. S. equation, and simulation data [40-43] for the compressibility factor \( Z^{FHS} \) of fluids of linear molecules consisting of equal fused hard spheres, the values of the ratio \( (Z_{m}^{sim} - 1)/(Z_{CS}^{CS} - 1) \) are determined as a function of the effective packing fraction \( y_{ef} \) for two and three center linear fused hard sphere fluids for several values of \( l \). It is found that the constancy of ratio \( (Z_{m}^{sim} - 1)/(Z_{CS}^{CS} - 1) \) for each shape holds within the accuracy, when known, of the simulation data, for all the cases considered at virtually all densities.

We can now test approximate result (3.55). However, instead of using the definition \( \alpha = R_m S_m/3V_m \), with \( R_m \), \( S_m \) and \( V_m \) the expressions corresponding to the real body [44], we use an alternative definition [39], better suited to the effective body:

\[ \alpha = \frac{1}{3\pi} \left( \frac{\partial v_m}{\partial \sigma} \right) \frac{\partial^2 v_m}{\partial \sigma^2} \frac{1}{V_m} \]

(3.59)
where, using expression (3.57) for the effective molecular volume, the partial
derivatives are given by [39]

$$\frac{\partial V_m^{\text{ef}}}{\partial \nu} = \frac{\pi \sigma^2}{2} \left[ 1 + \frac{5L}{2} - 3(n-1)\hbar \theta \frac{L^2 \theta}{4(n-1)\hbar} \right]$$  \hspace{1cm} (3.60)

and

$$\frac{\partial^2 V_m^{\text{ef}}}{\partial \sigma^2} = \pi \sigma \left[ 1 + 2L - 3(n-1)\hbar \theta \right] - \frac{3L^2 \theta}{8(n-1)\hbar} \frac{L^3}{16(n-1)^2 \hbar^2} + \frac{L^4 \theta}{32(n-1)^3 \hbar^3}$$  \hspace{1cm} (3.61)

From expressions (3.59–3.61) we can obtain values for an effective
value \(\alpha_{\text{ef}}\) corresponding to the shape factor of the effective body. Results,
reproduce the above mentioned constancy of the ratio \((Z_{\text{sim}} - 1)/(Z_{\text{CS}} - 1)\)
within error bars or, conversely, the equation of state put in the form

$$Z_{\text{FHS}} = 1 + \alpha_{\text{ef}} \left[ Z_{\text{CS}}(y_{\text{ef}}) - 1 \right]$$  \hspace{1cm} (3.62)

Agree with simulation data within the accuracy of the latter. In a
recent paper [45], the compressibility factor for the same type of fluids was
taken to be of the form

$$Z_{\text{FHS}} = 1 + c \left[ Z_{\text{CS}}(y) - 1 \right]$$  \hspace{1cm} (3.63)

which resembles equation (3.62) except for the fact that the packing
fraction \(y\) was used, instead of the effective packing fraction \(y_{\text{ef}},\) and \(c\) is an
adjustable parameter determined from the best fitting of equation (3.63) to the improved scaled particle theory (ISPT) equation [44]

\[ Z = 1 + (3\alpha - 2)y + \frac{(3\alpha^2 - 3\alpha + 1)y^2 - \alpha^2 y^3}{(1 - y)^3}, \]  

(3.64)

where the shape factor \( \alpha \) can be calculated analytically [45]. Although equation (3.64) was first derived for HCB fluids, it is also considered to be accurate for linear FHS fluids. With the values of \( c \) thus obtained, equation (3.63) provides similar results to those of equation (3.62) for low values of the bond length \( l \). For large values, however, the plot of \( (Z^{\text{FHS}} - 1)/(Z^{\text{CS}} - 1) \), as determined from simulation data \( Z^{\text{FHS}} \), shows a clear increase as the packing fraction \( y \) increases, and the deviation from constant \( c \) is greater than the uncertainty in the simulation data allows.

3.4 RELATION OF NON SPHERICITY PARAMETER WITH VIRIAL COEFFICIENTS

3.4.1 Introduction

So far, we have mainly focused on geometric quantities such as molecular volume \( (V_m) \) surface area \( (S_m) \) and mean curvature radius \( (R_m) \) in order to establish the elements of molecular shape within the theoretical description of HCB fluids. Especially among chemical engineers, it is common practice, however, to account for the effects of particle anisotropy in terms of dimensionless eccentricity parameters or shape factors. Adopting this view, we find that in case of pure fluids the equation of state depends on three
parameters. These are the reduced density or packing fraction $\eta$ and the shape factors $\alpha$ and $\tau$ respectively. For spherical molecules, the equation of state depends on the two parameters packing fraction $\eta$ and shape factor $\alpha$.

3.4.2 Theory

Two rigid convex molecules can, at most, be in contact at a single point and at that point the surface normal of the 1st molecule is anti – parallel to that of the second one. The volume excluded to the center of mass of the molecule, by the presence of the first, both molecules being held at fixed orientations, is called the excluded volume [46, 47]. The surface area $S_m$, the volume $V_m$ and the mean radius of curvature $R_m$ of convex molecules of several regular shapes are known [48, 36]. The average radius of curvature $R_{ex}$ the average surface area $S_{ex}$ and the average volume $V_{ex}$ corresponding to the excluded volume of hard convex molecule can be given in terms of its $R$, $S$ and $V$ through the use of the general formulas obtained by various workers [49–52]. On the other hand, Curtiss and Dahler [46] had obtained the expression for the surface and volume element of the excluded volume by introducing scaling parameters that smoothly varies from zero to unity. All the element ($R_m$, $S_m$ and $V_m$) are seensatially required in the study of thermodynamic properties of hard convex bodies.

A further attention concerns with the generalization of the Carnahan Starling equation with the eccentricity parameter ‘$\alpha$’ accounting for molecular anisotropy. This identification is indeed important, since it suggests a
promising route towards an improve description of thermodynamics of the hard convex molecules. In much the same spirit as Carnahan and Starling succeeded in approximately resuming the virial expansion for hard spheres, we might imagine the known results to fit the HCB virial expansion to the generalized Carnahan–Starling type expression.

\[
\frac{P}{\rho kT} = (1 - y)^{-3} \{1 + c_1 y + c_2 y^2 + c_3 y^3 + c_4 y^4 + \ldots \} \quad (3.65)
\]

The knowledge of the limited number of coefficients \(C_n\) should be sufficient in order to produce an accurate approximation to the HCB equation of state. Expanding equation (3.65) yields

\[
\frac{P}{\rho kT} = 1 + y(c_1 + 3) + y^2(c_2 + 3c_1 + 6) + y^3(c_3 + 3c_2 + 6c_1 + 10) + y^4(c_4 + 3c_3 + 6c_2 + 10c_1 + 15) + \ldots \quad (3.66)
\]

which should be compared to the virial series

\[
\frac{P}{\rho kT} = 1 + B_2^* y + B_3^* y^2 + B_4^* y^3 + B_5^* y^4 + \ldots \quad (3.67)
\]

In terms of \(C_n\) coefficients the reduced Virial coefficients

\[
B_m^* = \frac{B_m}{\langle V \rangle^{m-1}} \text{ are thus given by}
\]

\[
B_2^* = c_1 + 3 \quad (3.68)
\]

\[
B_3^* = c_2 + 3c_1 + 6 \quad (3.69)
\]
\[ B_4^* = c_3 + 3c_2 + 6c_1 + 10 \]  
\[ B_5^* = c_4 + 3c_3 + 6c_2 + 10c_1 + 15 \]  

Equation (3.68)–(3.71) clearly indicate that there are severe limitations as to the choice of appropriate analytical expressions for the \( C_n \) coefficients.

### 3.4.3 Derivation of Virial Coefficients

The argument is based on the configurational integral \( Q(N_1, \ldots, N_n, V) \) for an \( m \) component system of \( N \) particles of species I in volume \( V \). On the addition of a particle of characteristic radius \( R_j \) to the system, the configurational integral changes to \( Q(R_j, N_1, \ldots, N_m, V) \). For \( R_j \leq 0 \) this change can be readily evaluated as the volumes, from which particle \( j \) is excluded by the presence of other particles, do not overlap and the integration’s are trivial:

\[
\frac{Q(R_j, N_1, \ldots, N_m, V)}{Q(N_1, \ldots, N_m, V)} = \left(1 - \sum_{i=1}^{m} X_{ij} \frac{N_i}{V}\right)V,
\]

\[ (3.72) \]

where \( X_{ij} \) is the volume, averaged over all orientations, from which the center of particle \( j \) is excluded by particle \( i \). The work required to add particle \( j \) to the system is given by:

\[
\beta \omega(R_j) = -\ln \left(1 - \sum_{i=1}^{m} X_{ij} \frac{N_i}{V}\right).
\]

\[ (3.73) \]

The RFL theory assumes that \( \omega(R_j) \) can be represented for all values of
R_j by the first three terms of a Taylor series expansions about R_j = 0 plus a term V_{ij} is the volume of the particle j, that is:

\[ \omega(R_j) = \omega(0) + R_{j0}'(0) + \frac{R_j^2}{2\omega''(0)} + V_{jp}. \] (3.74)

This implies the continuity of \( \omega(R_j) \) for both positive and negative values of R_j. The term V_{jp} is introduced since at very large values of R_j and leading term in \( \omega(R_j) \) must be V_{jp}.

It remains to specify the excluded volumes X_{ij}. For hard spheres, the excluded volumes are:

\[ X_{ij} = \frac{4\pi}{3(R_j + R_i)^3} \] (3.75)

The more general case has been solved by Kihara and Hayashida [50, 53] and Kihara [51, 54] who showed that for any convex body:

\[ X_{ij} = V_i + V_j + \overline{R_i} S_j + \overline{R_j} S_i \] (3.76)

where S_i and V_i are the surface area and volume of particle i respectively and \( \overline{R_i} \) is the radius, averaged over all orientations, of particle i. The volume, surface area and average radius can be rewritten in terms of a characteristic radius or length for a particle as:
\[ V = c_i R_i^3, \]
\[ S = b_i R_i^2, \]
\[ R = a_i R_i. \]  

\[(3.77)\]

The values of \(a_i\), \(b_i\) and \(c_i\) for several shapes have been tabulated by Isihara and Hayashida [50, 53] and [51, 54]. If the expressions from equation (3.76) and (3.77) are substituted into equation (3.75) and the differentiation's carried out one finds that

\[
\beta \omega(R_j) = -\ln(1-y) + a_j R_j B(1-y) + \frac{b_j R_j^2 A}{(1-y)^2} + \frac{0.5a_j^2 R_j^2 B^2}{(1-y)^2} + V_{jp} \tag{3.78}
\]

where

\[
d = \sum_{i=1}^{m} d_i,
\]

\[
A = \sum_{i=1}^{m} a_i R_i d_i,
\]

\[
B = \sum_{i=1}^{m} S_i d_i,
\]

\[
C = \sum_{i=1}^{m} a_i^2 d_i,
\]

\[
Y = \sum_{i=1}^{m} V_i d_i.
\]
To obtain the chemical potential from this equation one has merely to add the ideal gas contribution:

\[ \beta_{ij} = \beta_0(R_j) + \ln \left( \frac{d_j h^3}{(2\pi m_j kT)} \right)^{3/2} \tag{3.79} \]

The equation of state can then be obtained from (3.79) and the thermodynamic equation:

\[ \frac{\partial P}{\partial d_k} = \sum_{i=1}^{m} d_i \frac{\partial \mu_j}{\partial d_k} \tag{3.80} \]

On carrying out the analysis for systems of particles with the same shape one obtains the equation:

\[ \beta P = \frac{d}{(1-y)} + \frac{1}{3} \frac{BC^2}{(1-y)^3} + \frac{AB}{(1-y)^2} \tag{3.81} \]

To check that the above equation is correct the values of \( a_i, b_i \) and \( c_i \) for a system of hard spheres were substituted into equation (3.81) and it was found that RFL or PY equation for mixtures was recovered (3.81). For a one component system equation (3.81) becomes, for \( j = 1 \):

\[ \frac{\beta P}{d_1} = \frac{1}{(1-V_1 d_1)} + \frac{1}{3} \frac{\bar{R}_1 S^2_1 d_1^2}{(1-V_1 d_1)^3} + \frac{\bar{R}_1 S L_1 d_1}{(1-V_1 d_1)} \tag{3.82} \]

If the values of \( a_i, b_i \) and \( c_i \), for a sphere are substituted into this equation, the PY equation is recovered.
By expanding equation (3.82) in powers of the density, the following expressions are obtained for the second, third and \( n \)th virial coefficients.

\[
B_2 = V_1 + R_1 S_1 \quad (3.83)
\]

\[
B_3 = V_1^2 + \frac{1}{3} \left( R_1 S_1 \right)^2 + 2V_1 S_1 R_1 \quad (3.84)
\]

\[
B_n = V_1^{n-1} + \frac{(n-1)! V_1^{n-3} S_1^2 R_1^2}{(n-3)! 3!} + (n-1) V_1^{n-2} R_1 S_1 \quad (3.85)
\]

The equation (3.83), (3.84) and (3.85) can also be written as

\[
B_2 = V(1+3\alpha) \quad (3.86)
\]

\[
B_3 = V^2 \left( 1 + 6\alpha + 3\alpha^2 \right) \quad (3.87)
\]

\[
B_n = V^{n-1} \left[ 1 + 3(n-1)\alpha + \frac{3(n-1)!}{2(n-3)!} \alpha^2 \right] \quad (3.88)
\]

3.4.4 Comparison of Approximate Virial Coefficients for Particles of Different Shapes

The results of Isihara et al. [50, 53]. Showed that the values of the second virial coefficients varied markedly with the shape of the particle. It is of interest therefore to compare the values of the virial coefficients for particles of different shapes with those of a hard sphere of the same volume. As noted previously the virial coefficients obtained from the PY equation for hard spheres are exact for the second and third virial coefficients and are very
good approximations for the fourth and fifth virial coefficients. The same
should therefore be true for non-spherical molecules.

The expression for $B_2$ in equation (3.83) agrees with the exact results
of Ishihara et al. [50, 53] Equation (3.84) also is exact for the third virial
coefficient of hard spheres. The values of the second, third, fourth and fifth
coefficients for some particles of arbitrary shape are compared with those for
hard spheres of equal volume in the table 3.1. Firstly it should be noted that
the virial coefficients for any other shape will always be greater than those of
hard spheres. This follows for the fact that for a sphere, the average radius
and surface area have minimum values for a body of given volume. From the
results in the table 3.1 it is apparent that the changes in the virial coefficients
are substantial and appear to increase with the order of the virial coefficient.
It would appear therefore that a non-spherical particle cannot be replaced by
an equivalent sphere which will give correct values of the virial coefficients
for all values of $n$. It is also noted that, for a large values of $n$, the second
term in equation (3.85) predominates and there is an equivalent sphere which,
for the limit of large $n$, can replace any particle. The values of the limits of
the ratios $B_n/B_n$ (HS) are tabulated in the table 3.1 for some shapes. This can
be important for systems at high density where the effect of the higher virial
coefficients is most important.
Table 3.1: Comparison of virial coefficients $B_n/B_n(\text{HS})$ for some shapes.

Comparisons were made at the same volume, not the same radius, for the particles.

<table>
<thead>
<tr>
<th>Body Characteristic lengths</th>
<th>Sphere $R$ (radius)</th>
<th>Cube $R$ (radius)</th>
<th>Cylinder $R$, $1 = 2R$ (radius) (length)</th>
<th>Regular Tetrahedron $R$ (side)</th>
<th>Ellipsoid $R$ (major semi-axis) $e^2=0.75$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average radius</td>
<td>$R$</td>
<td>$\frac{3}{4}R$</td>
<td>$(2+\pi)R/4$</td>
<td>$3/2\pi \tan^{-1}\sqrt{2R}$</td>
<td>$R(0.5)+\pi/\sqrt{2R}$</td>
</tr>
<tr>
<td>Surface area</td>
<td>$4\pi R^2$</td>
<td>$6R^2$</td>
<td>$6\pi R^2$</td>
<td>$\sqrt{3}R^2$</td>
<td>$2\pi R^2 (1.3800)$</td>
</tr>
<tr>
<td>Volume</td>
<td>$4\pi R^2/3$</td>
<td>$R^3$</td>
<td>$2\pi R^3$</td>
<td>$\sqrt{2}R^3/12$</td>
<td>$2\pi R^3/3$</td>
</tr>
<tr>
<td>$B_2/B_2(\text{HS})+$</td>
<td>1</td>
<td>1.375</td>
<td>1.2141</td>
<td>1.926</td>
<td>1.1345</td>
</tr>
<tr>
<td>$B_3/B_3(\text{HS})+$</td>
<td>1</td>
<td>1.675</td>
<td>1.3669</td>
<td>2.840</td>
<td>1.2349</td>
</tr>
<tr>
<td>$B_4/B_4(\text{HS})+$</td>
<td>1</td>
<td>1.8289</td>
<td>1.44176</td>
<td>3.4726</td>
<td>1.2701</td>
</tr>
<tr>
<td>$B_5/B_5(\text{HS})+$</td>
<td>1</td>
<td>2.0517</td>
<td>1.5919</td>
<td>4.0538</td>
<td>1.2964</td>
</tr>
<tr>
<td>$B_n/B_n(\text{HS})+$</td>
<td>1</td>
<td>2.25</td>
<td>1.6322</td>
<td>4.9868</td>
<td>1.3909</td>
</tr>
</tbody>
</table>

3.4.5 Theoretical Predictions of Virial Coefficients of HLTS Models

Recently Vega et al. [55] have determined the virial coefficients of the tangent hard spheres in the linear configuration and investigated the trends of the virial coefficients with the molecular anisotropy. Theoretical prediction of virial coefficients from different equations of state of hard body fluids are compared with the numerical results and found that none of them provides a completely satisfactory description of the lower virial coefficients when the anisotropy of the molecule is large.
The model of HLTS consists of m hard spheres in contact in a linear rigid configuration. Vega et al. [55] have evaluated the first six virial coefficients of HLTS with m ranging from m = 3 to m = 7 and proposed a relation between the virial coefficients and the non-sphericity parameter (α) by the empirical expression as

\[ B_i^* = C_0 + C_1\alpha + C_2\alpha^2 + C_3\alpha^3 + C_4\alpha^4 \]  

(3.89)

Here \( B_i^* = \frac{B_i}{V_{m-1}} \) is the reduced virial coefficient and \( B_i \) is the \( i^{th} \) virial coefficient.

It is found that the non-sphericity parameter α increases with the length of the molecules and the relation between α and m is roughly linear. It is also found that the virial coefficients are sensitive to the details of the shape for the larger value of α.

**Table 3.2:** Coefficients \( k_1, k_2 \) and \( k_3 \) of equation (3.90) for the EOS ISPT of [7] for the EOS proposed by Nezbeda [57] and the EOS proposed by Boublík [58].

<table>
<thead>
<tr>
<th></th>
<th>( k_1 )</th>
<th>( k_2 )</th>
<th>( k_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISPT</td>
<td>( 3\alpha - 2 )</td>
<td>( 3\alpha^2 - 3\alpha + 1 )</td>
<td>( -\alpha^2 )</td>
</tr>
<tr>
<td>Nezbeda</td>
<td>( 3\alpha - 2 )</td>
<td>( \alpha^2 + \alpha - 1 )</td>
<td>( -\alpha(5\alpha - 4) )</td>
</tr>
<tr>
<td>Boublík</td>
<td>( 3\alpha - 2 )</td>
<td>( 3\alpha^2 - 3\alpha + 1 )</td>
<td>( -\alpha(6\alpha - 5) )</td>
</tr>
</tbody>
</table>

Several EOSs have proposed for HLTS. Boublík [7] modified the
scaled particle theory of hard convex bodies of Gibbons [56] and proposed an improved version (ISPT). Later Nezbeda [57], by analyzing the virial coefficients of HSP models proposed a new EOS, which was slightly modified by Boublík [58]. These three EOSs are written in the form

$$Z = \frac{1 + k_1 y + k_2 y^2 + k_3 y^3}{(1 - y)^3} \quad (3.90)$$

where $y$ is the packing fraction defined as $y = \rho V_m$, and $\rho$ is the number density. The coefficients $k_1$, $k_2$ and $k_3$ are given in table 3.2 for the ISPT, Nezbeda and Boublík EOS. The virial coefficients obtained from equation (3.90) are given by

$$B_1^* = (k_2 + 3k_3) + 0.5(1 - k_1 - 3k_2 - 5k_3)i + 0.5(k_1 + k_2 + k_3)i^2 \quad (3.91)$$

In fact, equation (3.90) can be recovered by resummation of the Virial series with $B_1^*$ given by equation (3.91). It can be shown that for a hard convex body, the non-sphericity parameter [36, 59] defined by equation

$$B_2^* = 1 + 3\alpha^R$$

is given by

$$\alpha^B = \frac{RS}{3V_m} \quad (3.92)$$

where $R$ is $1/4\pi$ times the mean radius of curvature and $S$ is the surface – area of the molecule. For convex bodies equation $B_2^* = 1 + 3\alpha^R$ and equation (3.92) provide the same value of $\alpha$. For nonconvex bodies, for instance the
HLTS model, $R$ is ill defined. Boublík and Nezbeda [60] proposed for HLTS to take the mean radius of curvature from the corresponding HSP model with the same length to breadth ratio for HLTS equation $B_{2^*} = 1 + 3\alpha^R$ and equation (3.92) yield different values of $\alpha$, the difference being about 2% for $m = 3$ and 5% for $m = 7$.

Recently, another EOS has been proposed for HLTS by Wertheim [61] and independently by Chapman et al [10]. This EOS, which will be denoted by $W$, reads

$$Z = m \frac{(1 + y + y^2 - y^3)}{(1 - y^3)} - (m - 1) \frac{(1 + y - y^2/2)}{(1 - y)(1 - y/2)} \quad (3.93)$$

Following the work of Boublík [8], the equation (3.93) is recently modified to allow for overlapping of hard spheres. This modified version [61] of Wertheim’s EOS (MW) read

$$Z = (2\alpha^R - 1) \frac{(1 + y + y^2 - y^3)}{(1 - y^3)} - (2\alpha^R - 1) \frac{(1 + y - y^2/2)}{(1 - y)(1 - y/2)} \quad (3.94)$$

Equation (3.94) differs from that proposed by Boublík only in the way of defining $\alpha (\alpha^R$ in equation (3.94) instead of $\alpha^B$ which is the choice of Boublík). Equation (3.93) does not yield exact results for $B_{2^*}$ whereas equation (3.94) does. The virial coefficients obtained from equation (3.94) are

$$B_{2^*} = 1 + 3\alpha \quad (3.95)$$
\[ B_3^* = 14.5\alpha - 4.5 \]  
(3.96)

\[ B_4^* = 30.25\alpha - 12.25 \]  
(3.97)

\[ B_5^* = 50.125\alpha - 22.125 \]  
(3.98)

None of the presented EOSs yields completely satisfactory results for virial coefficients of HLTS and this is specially true for the highest elongations. The ISPT, the Nezeda and Boublík EOSs predict a linear variation in \( \alpha \) for \( k_1 \) and a quadratic dependence for \( k_2 \) and \( k_3 \) (see table 3.2). According to these three EOSs, \( B_1^* \) (except \( B_2^* \)) is a quadratic function of \( \alpha \).

All these three EOSs provide a fair prediction of \( B_3^* \). For \( B_4^* \) ISPT and Boublík EOSs fail because they give positive values of \( B_4^* \) when \( \alpha \to \infty \).

Only the Nezbeda EOS predicts negative values for \( B_4^* \) when \( \alpha \to \infty \) although the quantitative agreement is not very good. For \( B_5^* \), ISPT and Boublík EOSs capture the trends of the numerical results although they are not very precise.

The Nezbáda EOSs shows a maximum in \( B_5^* \) which is not observed in the numerical results. Equation (3.94) predicts that the virial coefficients are linearly increasing functions of \( \alpha \). The EOS provides good virial coefficients for HLTS up to \( \alpha = 2.5 \) (\( m = 4 \)) but it fails for higher values of \( \alpha \). In particular, this EOS is unable to predict negative values of \( B_4^* \) for very elongated molecules.
To summarized $B_3^*$ is well represented by a linear function of $\alpha$. $B_4^*$ by a quadratic function of $\alpha$ and $B_5^*$ as an increasing function of $\alpha$. None of the presented EOSs is able to reproduce all these features simultaneously. Furthermore, all these features are common for HLTS, HE and HSP models.

So for it has been focused that the variation of a given virial coefficients $B_i^*$ with the anisotropy (i.e. $\alpha$) for a given value of i. Now analyzing the variation of $B_i^*$ with i for a given molecule, $\alpha$ fixed, we find that the relation between $B_i^*$ and i is not linear for higher values of m. Thus the virial coefficient of Hard sphere fit relatively well to a quadratic form in i, for lower values of m, this fact justifies the success of Carnahan – Starling [62] EOS. However, the quadratic form cannot describe the presence of a maximum and a minimum in $B_i^*$ as a function of i.

Thus all the EOSs analyzed fail either in the prediction of variation of $B_i^*$ with $\alpha$ for a given i or in the variation of $B_i^*$ with i for a given $\alpha$. Although the error is small for medium anisotropies (and that explains their success in describing hard models of common molecules) it becomes more important for large anisotropies.

3.5 **INTEGRAL EQUATION THEORY**

3.5.1 **Introduction**

Polymer–RISM theory [63] is based on the RISM (Reference
interaction site model). The theory originally proposed by Chandler and Anderson [64-66], later on it worked out by Curro and Schweizer [63]. In polymer-RISM theory a perturbative scheme is used to reduce the RISM theory set of non-linear coupled integral equations for the individual site-site correlation functions, \( g_{ij}(r) \), to a single non-linear integral equation which related the average (over all sites) site-site total correlation function, \( h(r) = g(r) - 1 \), to the average site-site direct correlation function \( C(r) \), and the average site-site single chain distribution function, \( W(r) \). To solve the polymer RISM equation, in addition to a knowledge of \( W(r) \), another relation between the total and direct correlation functions, a “Closure” is required. In their work, Curro and Schweizer [67, 68] used a Percus–Yevick (PY) like closure to the polymer RISM equation. Comparing the predictions of their theory to Monte-Carlo simulations [69] it is found that the theory reproduced the local structure accurately beyond a distance of about 1.5 bead diameter but that at small distances the theory tended to significantly overestimate the value of the site-site distribution function \( g(r) \).

### 3.5.2 Polymer-RISM Theory

The original RISM theory of Chandler and co-workers [64-66] is based on the interaction site model for molecular fluids. In this model, each molecule is assumed to consist of a number of sites; the intermolecular potential \( u \) is assumed to be the sum of site-site potentials and is given by:

\[
  u(r) = \sum_{i<j} u_{ij}(r),
\]

(3.99)
where $u_{ij}$ is the potential between sites $i$ and $j$ on different molecules, and $r$ is the separation between the sites. In the freely jointed chain model, there are interaction sites located at the center of each of the $n$ hard spheres. The generalization of the Ornstein-Zernike (OZ) equation to molecules consisting of $n$ identical interaction sites is the size-site OZ (SSOZ) equation [64-66].

$$h_{ij}(r) = \int dr' \int dr \sum_{k,l=1}^{n} w_{ik}(r-r') c_{kl}(r'-r'') w_{lj}(r-r'')$$

$$+ \rho \int dr' \int dr \sum_{k,l=1}^{n} w_{ik}(r-r') c_{kl}(r'-r'') h_{lj}(r-r''), \quad (3.100)$$

where $\rho$ is the number density of molecules in the fluid, $h_{ij}(r)$ is the total site-site correlation function, $(h_{ij}(r) = g_{ij}(r) - 1)$, $g_{ij}(r)$ is related to the probability that sites $i$ and $j$ on different molecules are at a distance $r$ apart, $w_{ij}(r)$ is related to the probability that sites $i$ and $j$ on the same molecule are at a distance $r$ apart, and $c_{ij}(r)$ is the direct correlation function which is defined by Eq (3.100). For hard sphere site-site potentials, i.e.,

$$u_{ij} = \begin{cases} \infty & \text{if } r < \sigma \\ 0 & \text{if } r \geq \sigma \end{cases} \quad (3.101)$$

Eq. (3.100) may be closed with the relations,

$$h_{ij}(r) = -1, \quad r < \sigma, \quad (3.102)$$
\[ c_{ij}(r) = 0, \quad r > \sigma, \quad (3.103) \]

where \( \sigma \) is the distance of closest approach of any sites i and j. Equation (3.102) is an exact statement of the hard core conditions (3.101). Equation (3.103) is an approximation drawn from an analogy with the PY theory of hard spheres. The accuracy of this approximation may be judged by comparison with simulation data. Equations (3.100-3.103) are often referred to as the RISM equations. This system of order \( n^2 \) nonlinear coupled integral equations must be solved to obtain the local structure of a polyatomic fluid. For large \( n \) this becomes a difficult numerical problem.

Curro and Schweizer [63] using a perturbative scheme, reduced the set of \( n^2 \) equations given by eq. [3.100] to a single equation,

\[ h(r) = \int dr' \int dr'' w(r-r') c(r'-r'') \left[ w(r') + \rho_m h(r') \right] \quad (3.104) \]

where

\[ h(r) = \frac{1}{n^2} \sum_{ij} h_{ij}(r) \quad (3.105) \]

\[ c(r) = \frac{1}{n^2} \sum_{ij} c_{ij}(r) \quad (3.106) \]

\[ w(r) = \frac{1}{n} \sum_{ij} w_{ij}(r) \quad (3.107) \]
and \( \rho_m \) is the monomer (or site) density of the fluid, \( \rho_m = n \rho \). For molecules where all the correlation functions are identical, for example, in homonuclear diatomics and in ring-like chains, eq. (3.104) is identical to eq. (3.100). Equation (3.104) is referred to as the "polymer-RISM" equation. Polymer-RISM theory predicts the average \( g(r) \) as opposed to RISM, which predicts all of the individual \( g_{ij}(r) \). This is not a limitation, however, because \( g(r) \) is the quantity of interest for the thermodynamic properties such as the compressibility, and also for use in perturbation theories for chain fluids [70].

For chain fluids, eq. (3.104) can be viewed as an approximation where end effects are not explicitly incorporated, though they are included in \( w(r) \) via eq. (3.101) [63]. For hard chains, Curro and Schweizer [63] used a closure similar to eqs. (3.102) and (3.103)

\[
\begin{align*}
    h(r) &= -1, \quad r < \sigma, \\
    c(r) &= 0, \quad r > \sigma,
\end{align*}
\]  

(3.108)

(3.109)

Thus, given an expression for \( w(r) \), \( g(r) \) may be calculated for eqs. (3.104), (3.108) and (3.109). A number of approximations for \( w(r) \) have been suggested; in the work of Yethiraj and Hall [69]. They found that the approximation from the semiflexible chain model of Honnell et al. [71] was very accurate.

The polymer-RISM theory outlined above was able to accurately reproduce the local structure of the chain fluid (when compared to Monte Carlo simulations) except near contact, where the theory significantly
overestimated the value of \( g(r) \). A possible source of error in the theory is the closure for the direct correlation function, eq. (3.109).

Yethiraj and Hall investigated the accuracy of the closure, eq. (3.109) by calculating the \( c(r) \) that when input into the polymer-RISM equation, would give the \( g(r) \) observed in the simulation. Following Cummings et al. [72], Yethiraj and Hall rewritten the polymer-RISM equation (in Fourier space) as

\[
\hat{h}(k) = \hat{w}(k)\hat{c}(k)\hat{w}(k) + \rho_m \hat{w}(k)\hat{c}(k), \hat{h}(k) \tag{3.110}
\]

where the carets donate Fourier transforms. This can be rearranged to give

\[
\hat{c}(k) = \frac{\hat{h}(k)}{\hat{w}(k)\hat{w}(k) + \rho_m \hat{w}(k)\hat{h}(k)} \tag{3.111}
\]

Equation (3.111) expresses \( \hat{c}(k) \) in terms of \( \hat{h}(k) \) and \( \hat{w}(k) \), from simulation data for \( w(r) \) and \( g(r) \) we can calculate \( \hat{w}(k) \) and \( \hat{h}(k) \), and therefore \( \hat{c}(k) \). Numerical Fourier inversion of \( \hat{c}(k) \) gives \( c(r) \).

To improve the performance of polymer-RISM theory, the closure on \( c(r) \) outside the core is improved by replacing the PY-like closure of eq. (3.109), by a closure of the Yukawa form as,

\[
c(r) = K \frac{e^{-z[(r/\sigma)-1]}}{r}, \quad r > \sigma \tag{3.112}
\]

where \( K \) and \( z \) are unknown density-dependent parameters that must be
determined by forcing the theory to satisfy known thermodynamic relations. The shape of $c_e(r)$ suggests that this might be a good choice for $c(r)$ for $r > \sigma$. This closure, known as the generalized mean spherical approximation or the GMSA closure has been successful in the studies of hard spheres [73, 74] and homonuclear diatomic; [75] the extension to chain molecules is thus natural. In the study of hard spheres [73, 74] the parameters $K$ and $z$ were fixed by matching the theory's predictions for the virial pressure and the theory's predication for the compressibility pressure to an accurate equation of state.

3.5.3 Chiew Model

Equations for three intermolecular correlation functions for athermal hard sphere chain fluids are derived in the context of the Percus-Yevick (PY) integral equation theory. The approach employed here is based on a particle-particle description of chain molecular developed.

The quantity $g_{\alpha\beta}(r)$ is related to the probability of finding site $\alpha$ of a molecule and site $\beta$ of another molecule separated by a distance $r$. For long chains (e.g., polymers), it is appropriate to describe the structure of the molecules through so called average intermolecular correlation function $g(r)$ which is related to the site-site correlation $g_{\alpha\beta}(r)$ by

$$g(r) = \frac{1}{m^2} \sum_{\alpha=1}^{m} \sum_{\beta=1}^{m} g_{\alpha\beta}(r)$$  \hspace{1cm} (3.113)

here, $m$ represents the size or the number of hard sphere segments in the
chain molecule. The function $g(r)$ given the average probability of finding two sites in two different molecules separated by a distance $r$.

They derived a set of equations for the site-site total correlation function $h_{\alpha\beta}(r) = (g_{\alpha\beta}(r) - 1)$. For homonuclear hard sphere chain in the PY approximation, they then average the $h_{\alpha\beta}(r)$s to obtain equations for the single index average correlation function $h_{\alpha}(r)$ and the average total correlation function $h(r)$. It is found that the PY approximation does not provide a single closed equation governing the function $h(r)$. To calculate $h(r)$ additional information on the chain-end correlations are required. Two approximations which lead to the simplification of the PY results into a single equation for $h(r)$, are proposed and examined. Also, they obtained analytic expressions for these average correlation functions at contact, i.e., $g_\alpha(\sigma^+)$ and $g(\sigma^+)$. Furthermore, the functions $g_\alpha(r)$ and $g(r)$ are determined as a function of the total hard sphere site volume fraction $\eta$ and the chain length $m$. The PY results are then compared with the Monte-Carlo data [76] to determine the regime of validity of the approximation.

The particle-particle total correlation function $H_{ij}(r)$ between particles of species $i$ and $j$ in an N-component particle mixture follows the Ornstein-Zernike (OZ) integral equation [18, 70, 77, 78].

$$H_{ij}(r) = C_{ij}(r) + \sum_{k=l}^{N} \rho_k \int C_{ij}(s) H_{kj}(|r-s|) ds \quad (3.114)$$

In (3.114), the function $C_{ij}(r)$ represents the particle-particle direct
correlation function between particles with species i and j. To represent the athermal hard-sphere chain system considered here, they solved the OZ equation for the correlation functions $H_{ij}(r)$ and $C_{ij}(r)$ of an N-component particle mixture in the Percus-Yevick (PY) closure. The PY approximation provides the following boundary conditions to the OZ equation [79, 80], i.e., for $0 < r < \sigma_{ij}$,

$$H_{ij}(r) = -1 + \frac{\lambda_{ij} \sigma_{ij}}{12} \delta(r - \sigma_{ij})$$  \hspace{1cm} (3.115)

and for $r > \sigma_{ij}$,

$$C_{ij}(r) = 0$$  \hspace{1cm} (3.116)

Notice that, as before, the diameters of the hard-core particles are identical so that $\sigma_{ij} = (\sigma_i + \sigma_j)/2 = \sigma$. The short-ranged behaviour of $C_{ij}(r)$, given in (3.116) is consequence of the PY approximation of hard-core particles. The OZ equation subject to the above boundary conditions can be solved for through the use of the Weiner-Hopf factorization technique [81] to yield the following decoupled equation for $H_{ij}(r)$.

$$rH_{ij}(r) = -q_{ij}^0(r) + 2\pi \sum_{k=1}^{N} \rho_k \int_{S_{ij}} q_{ik}(r-t)H_{kj}(r-t)dt$$  \hspace{1cm} (3.117)

Here, the quantity $S_{ij} = (\sigma_i - \sigma_j)/2 = 0$ for particles with identical diameters $\sigma_i = \sigma$. The function $q_{ij}(t)$ is a short-ranged function which vanishes for $t > \sigma_{ij}$. In the range $S_{ij} < t < \sigma_{ij}$, it is given by
\[ q_{ij}(t) = \frac{a_i}{2} \left( t^2 - \sigma_{ij}^2 \right) + b_i (t - \sigma_{ij}) + \frac{\lambda_{ij} \sigma_{ij}}{12} \quad (3.118) \]

where

\[ a_i = \frac{1 - \xi_3 + 3 \sigma_i \xi_2}{(1 - \xi_3)^2} \frac{X_i}{(1 - \xi_3)} \quad (3.119) \]

\[ b_i = -\frac{3 \sigma_i^2 \xi_2}{2(1 - \xi_3)^2} + \frac{\sigma_i X_i}{2(1 - \xi_3)} \quad (3.120) \]

\[ X_i = \frac{\pi}{6} \sum_{k=1}^{N} \rho_k \lambda_{ik} \sigma_{ik}^2 \sigma_k \quad (3.121) \]

\[ \xi_i = \frac{\pi}{6} \sum_{k=1}^{N} \rho_k \sigma_k^4 \quad (3.122) \]

For the case considered here, the quantity \( \lambda_{ij} \neq 0 \) only if particles with species \( i \) and \( j \) constitute adjacent sites in the same chain molecule. Also, the summations in (3.117), (3.121) and (3.122) are taken over all particle species.

Following [80], the intermolecular site-site total correlation function \( h_{11}(r) \) of m-mer homonuclear chains (i.e., \( \sigma_i = \sigma \)) can be identified as the particle-particle total correlation function \( H_{1,m+1}^0(r) \). The function \( H_{1,m+1}^0(r) \) can be obtained by writing down the equation for the function \( H_{1,m+1}(r) \) explicitly from (3.117), followed by imposing the connectivity constraints to yield
\[ rH_{1,m+1}^0(r) = -q_1^*(r) + 12\eta_c \sum_{k=1}^{m} \int_0^{\sigma} q_1^*(t)(r-t)H_{k,m+1}^0(r-t)dt + \frac{1}{2} \int_0^{\sigma} (r-t)H_{2,m+1}^0(r-t)dt + \frac{1}{2} q_1^*(r-\sigma) \] (3.123)

Upon the application of the connectivity constraints, the function \( q_{ij}(t) \) in (3.118) becomes

\[ q_{ij}(t) = q_i^*(t) + \frac{\lambda_{ij}^0 \sigma^2}{12} \quad 0 < r < \sigma \] (3.124)

\[ = 0 \quad r > \sigma \] (3.125)

where

\[ q_i^*(t) = \frac{a_i^*}{2} (t^2 - \sigma) + b_i^* (t-\sigma) \quad 0 < r < \sigma \] (3.126)

\[ = 0 \quad r > \sigma \] (3.127)

The quantities \( a_i^* \) and \( b_i^* \) are given by

\[ a_i^* = \frac{(1+5\eta)}{2(1-\eta)^2} \] (3.128)

\[ b_i^* = \frac{(1-7\eta)}{4(1-\eta)^2} \] (3.129)

if the index \( i \) represents a terminal site in the chain molecule, and
\[ a_i = \frac{3\eta}{(1-\eta)^2} \]  
(3.130)

\[ b_i = \frac{(1-4\eta)}{2(1-\eta)^2} \]  
(3.131)

if the index i represents a non-terminal site. In equations (3.128-3.131) as before, the quantity \( \eta \) denotes the total volume fraction of the hard-sphere sites. Although (3.123) is written down for the particle-particle total correlation function \( H_{1,m+1}^0(r) \), it can be equivalently expressed as the molecular site-site total correlation function \( h_{11}(r) \), i.e.,

\[
r_{h_{11}}(r) = -q_i^*(r) + 12\eta \sum_{\gamma=1}^m \int_0^\sigma q_i(t)(r-t)h_{\gamma 1}(r-t)dt \\
+ \frac{1}{2} \int_0^\sigma (r-t)h_{21}(r-t)dt + \frac{1}{2} q_i^*(r-\sigma) \]  
(3.132)

3.5.4 Average Correlation Function \( g(r) \)

The equation for the average total correlation function \( h(r) (= g(r) - 1) \) is now derived. This is accomplished by averaging the total correlation functions \( h_\alpha(r) \) over all sites \( \alpha \) through \( h(r) = \frac{1}{m} \sum_{\alpha=1}^m h_\alpha(r) \)

\[
rh(r) = -Q^*(r) + 12\eta \int_0^\sigma dtQ^*(t)(r-t)h(r-t) + \frac{m-1}{m} Q^*(r-\sigma) \\
+ \int_0^\sigma dt(r-t)h(r-t) - \frac{1}{m} \int_0^\sigma dt(r-t)h_{11}(r-t) \]  
(3.133)
Here, the function $Q^*(r)$ is defined as

$$Q^*(r) = \frac{1}{m} \sum_{\gamma=1}^{m} q_{\gamma}^*(r)$$

(3.134)

where $q_{\gamma}^*(r)$ is given by (3.126) and (3.127). Based on the procedure used in obtaining $g_2(\sigma^+)$, an analytic expression for the PY contact value of $g(\sigma^+)$ can be obtained from (3.133). It is found

$$g(\sigma^+) = \frac{2 + (3m - 2)\eta}{2m(1 - \eta)^2}$$

(3.135)

A key feature to be noted in (3.133) is that the Percus-Yevick approximation does not yield a closed equation for the average total correlation function $h(r)$. The computation of $h(r)$ requires additional information on the chain end correlation in the form of $h_1(r)$ (as seen in the last term of (3.133). An inspection of (3.133) shows that the contribution of $h_1(r)$ diminishes with increasing chain length $m$, and vanishes in the limit of $m = \infty$. This is consistent with the physical behaviour of chain molecules in that chain-end effects decreases as the chain length of the molecules increases. Thus, a 'full-PY' solution of $h(r)$ or $g(r)$ requires information on the single index average site-site correlation function $h_1(r)$ which must be determined separately before $h(r)$ can be solved from (3.133). This means that the calculation of $h(r)$ requires the simultaneous solution of $m$ equations for $h_\alpha(r)$. Hence, it is of interest to invoke further assumptions beyond the approximate PY theory to derive a single closed equation for $h(r)$. 
3.5.5 PY1 Approximation

Two approximations beyond the PY theory are considered. They will be referred to as PY1 and PY2 solutions. In the PY1 approximate scheme, the last term on the right-hand side of (3.133), which involves the single index function \( h_1(r) \) is ignored completely. Equation (3.133) reduced to

\[
\begin{align*}
\rho h(r) &= -Q^*(r) + 12\eta_c \int_0^\sigma dt Q^*(t)(r-t)h(r-t) + \frac{m-1}{m} Q^*(r-\sigma) \\
&+ \int_0^\sigma dt(r-t)h(r-t)
\end{align*}
\]

(3.136)

The magnitude of the last term on the right-hand side of (3.133) decreases with increasing \( m \), and vanishes in the limit \( m \to \infty \), thus the error introduced in (3.136) will decrease as \( m \) increases. The PY1 approximation is not expected to yield accurate values for \( h(r) \) for short chains, and will approach the ‘full-PY’ solution for large \( m \).

3.5.6 PY2 Approximation

In the PY2 approximation, it is assumed that all segments in the chain molecules are equivalent to each other so that \( h_1(r) = h_2(r) = \ldots = h_m(r) = h(r) \). Hence, in this approximation, the function \( h_1(r) \) in (3.133) is replaced with \( h(r) \) to yield a single closed equation for \( h(r) \).

\[
\begin{align*}
\rho h(r) &= -Q^*(r) + 12\eta_c \int_0^\sigma dt Q^*(t)(r-t)h(r-t) + \frac{m-1}{m} Q^*(r-\sigma)
\end{align*}
\]
\[ + \frac{m-1}{m} \int_0^\infty \delta(t) \varphi(r-t) \, dt \]  

(3.137)

The assumption that all sites are equivalent (in an average sense) does not hold for short chains but is expected to be a good approximation for long polymeric chain.

The PY theory is found to yield accurate values for \( g(\sigma^+) \) at small \( \eta \). It is found that the PY theory does not yield a closed equation for the average total correlation function \( h(r) \). Solving \( h(r) \) requires additional information on the chain end correlation functions. Two approximations (beyond PY theory) which yield a single closed equation for \( h(r) \) are proposed and examined. Analytic expressions for these average correlation functions at contact are obtained as a function of the chain length \( m \) and hard-sphere site volume fraction \( \eta \). Numerical solutions for \( g(r) \) are obtained for 4-mer and 8-mer chains and compared with computer simulation data. It is found that the PY theory is able to predict \( g(r) \) for 4-mer chains accurately. However, only qualitative agreement is obtained for 8-mer chains.

3.6 THERMODYNAMIC THEORY

3.6.1 Introduction

The statistical thermodynamics for fluids of molecules which interact by the forces of chemical binding type are studied in this chapter. Such forces are modeled by molecules consisting of hard cores with embedded attraction sites. The range of attraction between sites in different molecules is chosen to
be sufficiently short so that double bounding of sites is precluded. The condition for this to be valid with spherical cores has been noted elsewhere [26, 82].

The number of molecular attraction sites control the physical behaviour. Molecular models with one site allow only dimerization. The presence of two sites permits the formation of chain and ring polymers. Additional sites allow formation of branched polymers and amorphous system.

There is a fixed angle 'α' between the vectors from the center of the hard core to the two attraction sites [23]. The thermodynamics as predicted by Thermodynamic Perturbation Theory (TPT), however, is independent of α [23]. This is certainly incorrect if α lies in the physically unreasonable range of small angles, where the hard cores prevents simultaneous bonding of both sites of a bead. That is why the two closely related problems of the limits of validity of TPT, and the correct extension to flexible chains are investigated. The lowest order TPT result is indeed valid for both rigid and flexible chains, while a small difference arises in second - order TPT. The case of unphysical α is should to be amenable to a resummation technique which recovers correct results and makes the physical situation quite transparent.

The simulation results with first and second - order TPT, finding generally good agreement in First order, with a slight improvement in going to the Second order. The magnitude of discrepancy increases with chain
length, indicating the extrapolation to very long chains is unjustified.

### 3.6.2 Pair Potential in TPT

A model potential capable of representing a wide variety of physical circumstances is the following:

\[
\phi(12) = \phi_R(12) + \sum_\alpha \sum_\beta \phi_{\alpha \beta} \left( |r_{12} + d_\alpha(\Omega_i) - r_1 - d_\beta(\Omega_j)| \right) \tag{3.138}
\]

where \( i = 1, 2, \ldots \) is shorthand for the position \( r_1 \) of the molecular center and the orientation \( \Omega_i \) of molecule \( i \); \( d_\alpha \) and \( d_\beta \) are vectors from the molecular center to an interaction site. The \( \phi_{\alpha \beta} \) between pairs of sites in distinct molecules are assumed to be attractive, i.e., \( \phi_{\alpha \beta} \leq 0 \). The potential \( \phi_R(12) \) is taken to be the interaction of two hard particles of given shape, or at least strongly repulsive. The simplest example is the hard sphere potential.

\[
\phi_R(12) = \begin{cases} 
\infty & \text{for } r_{12} < D \\
0 & \text{for } r_{12} > D 
\end{cases} \tag{3.139}
\]

where \( D \) is the hard sphere diameter.

M.S. Wertheim specializes to a one-component system of molecules with a single attraction site. Even this reflects a wide range of physical situations. If the site coincides with the center of isotropic repulsion then we have a simple fluid, which exhibits the usual gas-liquid transition. The simplest model consists of hard sphere \( \phi_R(12) \) given by (3.139) and a \( \phi_A(12) \) of finite range:

104
\[
\phi_A(x) = \begin{cases} 
< 0 & \text{for } x < a \\
0 & \text{for } x > a
\end{cases}, \quad x = r_2 + d(\Omega_2) - r_1 - d(\Omega_1) \tag{3.140}
\]

where \( d \) must satisfy

\[
\frac{1}{2}(D - a) < d < \frac{1}{2}D \tag{3.141}
\]

The case of a site of short-ranged attraction located near the edge of the hard core is realized by the additional restriction.

\[a \ll D \tag{3.142}\]

This has the following consequences. In any allowed configuration of any number \( N \) of molecules, each particle can take part in only one attractive interaction \( \phi_A(ij) \neq 0 \). If this is satisfied for the pair \( (ij) \), then the repulsive cores of \( i \) and \( j \) prevent any particle \( k \) from coming close enough to feel the influence of the attraction sites of \( i \) or \( j \). Interactions of this type were first considered by Anderson [83, 84].

In theories formulated in terms of graphs, \( \phi_R(12) \) appears in the form of the Mayer \( f \)-function, defined by

\[
e(12) = \exp[-\beta \phi(12)], \quad f(12) = e(12) - 1 \tag{3.143}
\]

Here \( \beta = 1/kT \), where \( k \) is Boltzmann’s constant and \( T \) is the Kelvin temperature. The usual standard decomposition is

\[
f(12) = f_R(12) + F(12), \quad F(12) = e_R(12)f_A(12) \tag{3.144}
\]
3.6.3 Formulation of TPT

The reformulated statistical thermodynamics [23] is based on introducing separate singlet densities for each possible bonding state of a molecule. Here the four singlet densities are $\rho_0$, $\rho_A$, $\rho_B$, and $\rho_{AB}$, where the subscript identifies the bounded sites. The actual calculations are more convenient in terms of parameters $\sigma_0$, $\sigma_A$, $\sigma_B$, and $\sigma_r$, related to the $\rho$'s by

$$
\sigma_0 = \rho_0, \quad \sigma_A = \rho_A + \rho_0, \quad \sigma_B = \rho_B + \rho_0,
$$

(3.145)

$$
\sigma_r = \rho_{AB} + \sigma_A + \rho_B + \sigma_0 = \rho,
$$

(3.146)

where $\rho$ is the total singlet density for all bonding states.

The difference between the Helmholtz free energies $A$ of the real system, and $A_R$ of the reference system, was found to be [23]

$$
\beta(A - A_R) = \int \left( \sigma_r(1) \ln \frac{\sigma_0(1)}{\sigma_r(1)} + \sigma_r(1) - \sigma_A(1) - \sigma_B(1) + \frac{\sigma_A(1) \sigma_B(1)}{\sigma_0(1)} \right) \text{d}(1) - c^{(0)} + c_R^{(0)}
$$

(3.147)

Hence, $c^{(0)}$ is the sum of all irreducible graphs on field (integrated) points. The possible connectors of a pair of points $i,j$ are $f_R(ij)$, $F_{AB}(ij)$ and $F_{BA}(ij)$. Each site is bonded at most once. A point $i$ carries a factor $\sigma_Q(i)$, where $Q$ is the complement of the set of bonded sites at $i$. The subset of graphs with only reference system bonds $f_R(ij)$ is $c_R^{(0)}$; all its points carry a
factor \( \sigma_r(i) = \rho(i) \). We can condense the graphs in

\[
\Delta c^{(0)} = c^{(0)} - c_R^{(0)}
\]

(3.148)

by means of reference system correlation functions \( g_s(1, \ldots, s) \). Then only points with incident attraction bonds are left, and dependence of \( \Delta c^{(0)} \) on \( \sigma_r = \rho \) is absorbed completely into the reference system correlations.

The chemical equilibrium conditions that establish the self-consistent values of \( \sigma_0, \sigma_A, \) and \( \sigma_B \) are equivalent to stationarity of \( A-A_R \) with respect to these parameters; this is a consequence of a minimum principle for \( A \). By functional differentiation this means,

\[
\frac{\sigma_B(1)}{\sigma_0(1)} - 1 = \frac{\partial \Delta c^{(0)}}{\partial \sigma_A(1)}
\]

(3.149)

and similarly with \( A \) and \( B \) interchanged, and

\[
\frac{\sigma_A(1)}{\sigma_0(1)} \frac{\sigma_B(1)}{\sigma_0^2(1)} = \frac{\partial \Delta c^{(0)}}{\partial \sigma_0(1)}
\]

(3.150)

An expression for the pressure \( p \) is based on the relation

\[
pV = G - A = \int \sigma_\Gamma(1) \frac{\partial A}{\partial \sigma_\Gamma(1)} d(1) - A,
\]

(3.151)

where \( V \) is the volume of the system, and \( G \) is the Gibbs free energy. When this is applied to the difference \( A-A_R \), the result is
\[ \beta(P - P_R)V = \int \left( -\sigma_\Gamma(1) + \sigma_A(1) + \sigma_B(1) - \frac{\sigma_A(1)\sigma_B(1)}{\sigma_\Gamma(1)} \right) d(1) \]

\[ + \Delta c^{(0)} - \int \sigma_\Gamma(1) \frac{\partial \Delta c^{(0)}}{\partial \sigma_\Gamma(1)} d(1) \]  

(3.152)

Previously we considered only the lowest-order TPT, which consists of retaining only the two-point graph in \( \Delta c^{(0)} \). In this approximation

\[ \Delta c^{(0)} = \int \sigma_A(1) \sigma_B(2) g(12) F_{BA}(12) d(1) d(2) \]  

(3.153)

This first-order TPT predicts an equation of state which is in remarkable agreement with DH simulation of flexible bead oligomers of fixed bead number. Furthermore, it is not practical to go beyond second-order TPT, because of our ignorance of reference system correlations beyond our scanty knowledge of \( g(123) \). Nevertheless, it is appropriate to choose a somewhat more general starting point in order to understand the success of TPT, to assess the limits of its validity, and to understand the modifications required the limit of validity is exceeded.

3.6.4 Chain Approximation

The main aim is the calculation of the equation of state in first- and the second-order TPT for both rigid and flexible chains. The latter case is then to be compared to the DH simulation of flexible chains with a fixed number of beads.

We start with the calculational simplification which arises from the
more general approximation of retaining only graphs with a single chain of attraction bonds. This implies that the approximate \( \Delta c^{(0)} \) is linear in \( \sigma_A \) and \( \sigma_B \), so that we have

\[
\Delta c^{(0)} = \int \sigma_G (l) \frac{\partial \Delta c^{(0)}}{\partial \sigma_G (l)} d(l) \quad \text{for} \quad G = A \text{ or } B. \tag{3.154}
\]

We can use this and eq. (3.149) in eq. (3.152) to obtain simpler expression for the pressure, namely,

\[
\beta (P - P_R) V = \int \left[ -\sigma_T (l) + \sigma_G (l) \right] d(l)
\]

\[
- \int \sigma_T (l) \frac{\partial \Delta c^{(0)}}{\partial \sigma_T (l)} d(l) \tag{3.155}
\]

Furthermore, it is defined

\[
\nu = \frac{\bar{\sigma}_T}{\bar{\sigma}_G}, \quad \tau = \frac{\bar{\sigma}_G}{\bar{\sigma}_0} \tag{3.156}
\]

where \( \bar{\sigma}_G = \bar{\sigma}_A = \bar{\sigma}_B \). As previously noted \( \nu \) is the mean number of beads per chain.

(a) **First-order TPT**

The equation of state is obtained from eqs. (3.149), (3.150) and (3.152). In first-order TPT only \( I_1 \) is retained and thus we find

\[
\tau - 1 = \bar{\sigma}_G I_1 \tag{3.157}
\]
\[ \nu - \tau = 0 \]  \hspace{1cm} (3.158)

\[ \beta(p - p_R)/\bar{\rho} = -1 + \frac{1}{\nu} - \frac{\sigma_g}{\nu} \bar{I}_1' \]  \hspace{1cm} (3.159)

where \( I_1 = \Omega^{-1} \int g(12)f_{AB}(12)d(2) \)  \hspace{1cm} (3.160)

and the prime denotes differentiation with respect to \( \bar{\rho} = \bar{\sigma}_g \). By the use of eqs. (3.156) and (3.157) this becomes

\[ \beta(p - p_R)/\bar{\rho} = (-1 + \nu^{-1})(1 + \bar{\rho}l'_1/I_1) \]  \hspace{1cm} (3.161)

This form is chosen in order to eliminate the strength parameter K in the glue spot limit, where

\[ I_1 = Kg(D) \]  \hspace{1cm} (3.162)

where \( D \) is the hard sphere diameter. The reference system quantities are well approximated by the Carnahan-Starling equation of state, and a value of \( g(D) \) consistent with it,

\[ \frac{\beta p_R}{\bar{\rho}} = \left( 1 + \eta + \eta^2 - \eta^3 \right)/(1 - \eta)^3, \]  \hspace{1cm} (3.163)

\[ g(D) = (1 - \frac{1}{2}\eta)/(1 - \eta)^3, \]  \hspace{1cm} (3.164)

where \( \eta = \pi \bar{\rho} D^3/6 \). The first-order TPT yields the equation of state
\[
\frac{\beta p_R}{\bar{\rho}} = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3} \left(1 - \frac{1}{\nu} \right) \left(1 - \frac{\eta}{2-\eta} + \frac{3\eta}{1-\eta} \right)
\] (3.165)

In the glue spot limit, \( \bar{\rho} \) and \( \nu \) are appropriate independent variables.

When the TPT equation of state is compared with the Monte Carlo results of Dickman and Hall [85], equating mean number of beads \( \nu \) to their fixed number \( N \), the overall agreement is very good, considering the extended density range. Dickman and Hall compared four theories, including two that they have devised. With the identification \( N = \nu \), TPT and the two DH theories share the feature that \( \beta p/\rho_p \) consists of a linear term in \( N \) and a term independent of \( N \). The DH theories give qualitatively similar behavior, but TPT yields the best overall agreement.

Nevertheless, the simulations for \( N = 4, 8, \) and 16 show that the discrepancy between simulation and TPT increases with \( N \), so that extrapolation to very large \( N \) is certainly unjustified. For this reason, it becomes interesting to investigate higher orders of TPT.

(b) **Second-order TPT**

In second order, eqs. (3.157) - (3.159) are replaced by

\[
\tau - 1 = \bar{\sigma}_G (l_1 + \bar{\sigma}_0 l_2) \quad (3.166)
\]

\[
\nu - \tau = \bar{\sigma}_G \bar{\sigma}_0 l_2, \quad (3.167)
\]
\[ \beta(p - p_R) = -1 + \nu^{-1} - \sigma_G^2(I_1' + \sigma_0'I_2') \] (3.168)

where \[ I_2 = \Omega^{-1} \int G(123)f_{AB}(12)f_{AB}(23)d(2)d(3) \] (3.169)

We can obtain \( \tau \) in terms of \( \nu, I_1, \) and \( I_2 \) as follows. From eqs. (3.166) and (3.167) we obtain

\[ 2\tau - \nu - 1 = \int_{G} I_1', \quad \tau(\nu - \tau) = \sigma_G^2 I_2 \] (3.170)

Elimination of \( \sigma_G \) leads to

\[ (2\tau - \nu - 1)^2 \lambda = \tau(\nu - \tau), \quad \lambda = I_2^2 / I_1^2 \] (3.171)

Note that, in the glue spot limit, \( \lambda \) is independent of the strength parameter \( K \).

The quadratic equation for \( \tau \) has the solution:

\[ \tau = \frac{\nu(1 + 4\lambda) + 4\lambda + \left[ \nu^2 (1 + 4\lambda) - 4\lambda \right]^{\frac{1}{2}}}{2(1 + 4\lambda)} \] (3.172)

By eliminating \( I_2 \) in favor of \( \lambda \) in eq. (3.168) and requiring the appearance of \( I_1' \) in the form \( I_1'/I_1 \), eq. (3.168) is reduced to the form

\[ \frac{\beta(p - p_R)}{\rho} = \left( -1 + \frac{1}{\nu} \right) \left( 1 + \frac{\bar{\rho}l_1'}{l_1} \right) - \frac{\nu - \tau \bar{\rho}l'}{\lambda} \] (3.173)

In this convenient form the difference between TPT 1 and TPT 2 is the term in \( \bar{\rho}l'/\lambda \). Its coefficient can be rewritten in terms of \( \nu \) and \( \lambda \) as
\[
\frac{\nu - \tau}{\nu} = \frac{1}{2} \left( 1 + 4\lambda - 4\lambda \nu^{-2} \right)^{1/2} - \frac{2\lambda}{2(1 + 4\lambda)(1 + 4\lambda) \nu} \tag{3.174}
\]

Anticipating the fact that \(\lambda\) turns out to be small compared to 1, we have for small \(\lambda\),

\[
\frac{(\nu - \tau)}{\nu} = \lambda \left( 1 - \nu^{-1} \right)^2 + O(\lambda^2) \tag{3.175}
\]

In the following evaluation of \(\lambda\) we assume that \(\xi(\alpha)\) vanish in the region \(\alpha < \pi/3\) and that the system is one of hard spheres with glue spots.

For fixed bond angle \(\alpha\) we have

\[
\lambda = \frac{g(D, D, 2D \sin \frac{1}{2} \alpha)}{g^2(D)} - 1 \tag{3.176}
\]

where the arguments of the hard sphere triplet distribution function are the three center-to-center distances. In the flexible case this becomes

\[
\lambda = \int_{\pi/3}^{\pi} \left( \frac{g(D, D, 2D \sin \frac{1}{2} \alpha)}{g^2(D)} - 1 \right) \xi(\alpha) \sin \alpha d\alpha \tag{3.177}
\]

The totally flexible case is represented by

\[
\xi(\alpha) = \begin{cases} 
0 & \text{for } 0 < \alpha < \pi/3 \\
2/3 & \text{for } \pi/3 < \alpha < \pi 
\end{cases} \tag{3.178}
\]

so that
\[ \lambda = \frac{2}{3} D^{-2} \int_D^{2D} \left[ g(D, D, x)/g^2(D) - 1 \right] x \, dx \quad (3.179) \]

There is strong cancellation between the two terms in the integrand. The Kirkwood superposition approximation is, of course, quite useless, because it is bad in the lowest non-vanishing order, consisting of graphs with one field point. Here superposition retains one graph, but neglects a comparable one of opposite sign. We do have two sources of useful information. The first one is the computer simulation of Uehara et al. [86] who tabulate values of \( g(D, D, x) \) for two densities, \( \eta = 0.2222 \) and \( 0.2755 \). From these values we can calculate \( \lambda \) with an uncertainty of several percent.

A second source is the limit \( \eta = 0 \), where the lowest order may be calculated analytically, using integration methods used in another connection [87]. After a very long analytic calculation he found that in lowest order

\[ \lambda = \left( \frac{12 \arccos(1/3)}{5\pi} - \frac{8\sqrt{2}}{15\pi} - \frac{7}{15} \right) \eta = 0.233633\eta \quad (3.180) \]

The two values of \( \lambda(\eta) \) obtained from the work of Uehara et al. [86] and the initial slope from eq. (3.180) could be fitted by the quadratic fitting function

\[ \lambda = 0.233 \, 633\eta(1+1.482\eta) \quad (3.181) \]

This fitting function was used to calculate the equation of state in second-order TPT. The difference between TPT 1 and TPT 2, is very small.
This was shown by a tabular comparison between TPT 1 and TPT 2 at the actual simulation densities of Dickman and Hall [85] by Wertheim [61].

(c) **Validity of TPT**

The first-order TPT, retaining the single graph described by eq. (3.154), there is no dependence on the bond angle $\alpha$, as noted previously [23]. This is reason for concern, since it is clearly wrong in the rather unphysical case of small $\alpha$. For the sake of concreteness, consider the model of hard spheres with surface glue spots A and B. Here polymerization can occur only for $\alpha > \pi/3$. For $\alpha < \pi/3$, bonding of one site blocks bonding of the other, so that only dimers are formed. In TPT, an indication of the change in behavior is seen as soon as we go to second-order TPT, retaining the chain of attraction bonds on three points. Analytically, this term in $\Delta c^{(0)}$ is expressed as

$$
\int \sigma_A(1) \sigma_0(2) \sigma_B(3) f_{BA}(12) f_{BA}(23) G(123) d(1)d(2)d(3)
$$

(3.182)

where

$$
G(123) = g(123) - g(12)g(23)
$$

(3.183)

This is an example of a more general result for chains on s points,

We rearrange the factors $G(123)$ as follows:

$$
G(123) = E(123) + g(12)g(23)f_R(13)
$$

(3.184)

where
\[ E(123) = g(123) - g(12)g(23)e_R(13) \quad (3.185) \]

The difference between the two ranges of bond angle is now obvious. In the physically reasonable case \( \alpha > \pi/3 \), the term with \( f_R(13) \) vanishes, because \( f_R(13) = 0 \) in the bonded configuration. The term in \( E(123) \) contributes, but is expected to be small. \( E(123) = 0 \) is an exact result for the linear ordering 1, 2, 3 in one-dimensional systems [88]. In three dimensions, an approximation of this type underlies the reasonably successful Percus shielding approximation [89, 90] for the density profile of hard spheres near a hard wall.

For \( \alpha < \pi/3 \), the situation is reversed. In the bonded configuration the enforced overlap of the cores of 1 and 3 results in \( E(123) = 0 \). The term in \( f_R(13) \), on the other hand, has \( f_R(13) = -1 \).

Using \( Q \) as a generic subscript for any of the four species, we denote the number densities by \( \rho_Q = \rho_Q(1)\Omega \), where \( \Omega = 8\pi^2 \) is the integral over orientations. Similarly \( \sigma_Q = \sigma_Q(1)\Omega \). In the approximation of retaining only chains we have

\[
\Delta e^{(0)}/V = \sigma_A \sigma_B \sum_{n=0}^{\infty} \frac{-\rho}{\rho_0 I_{n+1}}, \quad (3.186)
\]

where \( I_n \) is the integral with a chain of \( n \) links. For \( n = 1 \) and 2, we have

\[
I_1 = \Omega^{-1} \int g(12)f_{AB}(23)d(2) \quad (3.187 \text{A})
\]
\[ I_2 = \Omega^{-2} \int G(123) f_{AB}(12) f_{AB}(23) d(2) d(3) \] (3.187 B)

As long as \( e_R(13) = 0 \), i.e., the cores of 1 and 3 overlap, for all configurations such that both bonds are unbroken, we have the unphysical situation with

\[ G(123) = -g(12)g(23), \] (3.188)

and as a result \( I_2 \) becomes the product of two independent integrals, namely,

\[ I_2 = -I_1^2 \] (3.189)

Thus the series of \( \Delta c^{(0)} \) begins

\[ \Delta c^{(0)}/V = \overline{\sigma}_A \overline{\sigma}_B (I_{1-} \overline{\sigma}_0 I_1^2 + \ldots..), \] (3.190)

Here the second term in general is not small compared to the first, and the form of eq. (3.190) suggests that resummation is feasible and required.

3.7 **EQUATIONS OF STATE FOR CHAIN MOLECULES**

3.7.1 **Flory and Flory-Huggins Theories**

(a) **Introduction**

In this chapter, the equations of state for fluids of chain molecules are derived as generalization of the well known Flory and Flory-Huggins lattice theory to continuous space, which provided an accurate prediction for the pressure over a wide range of densities:
Fluids composed of chain molecules are of increasing interest, owing to their richly varies static and dynamic properties. While the techniques commonly employed in theories of simple liquids have been intended to the molecular fluid, such approaches often pose formidable computational difficulties when applied to the chain molecules. To overcome these difficulties when applied to the chain molecules, two mean field theories have been developed; Flory Theory (F) and Flory-Huggins (FH) Theory [91, 92].

The original F and FH arguments appealed to a lattice picture for estimating the number of configurations, but certain of the resulting expressions are free of lattice related parameters and would appear to be applicable to continuous space systems. F and FH theory in particular the equation of state-betray, in their basic structure. The predictions of the continuous space version of mean fluid theory for higher densities have been investigated.

(b) **Lattice Model**

Dickmann and Hall [93] considered chain of n segments on a lattice, which interact via a pairwise segment-segment interaction. The intramolecular contribution to the potential energy may also depend on the relative orientation of successive bonds. We write the total potential energy of a system of \( N_p \) chains as

\[
U_{N_p} = \frac{1}{2} \sum_{i \neq j} \sum_{k,j=1}^n u(x_i^{(k)} - x_j^{(l)}) + \sum_{i=1}^M w(x_i^{(0)}, \ldots, x_i^{(n)}) \tag{3.191}
\]
where \( x_i^{(k)} \) denotes the position of the \( k \)th segment of the \( i \)th chain. Dickman and Hall assumed that \( u = u_0 + u' \) and \( v = v_0 + v' \), where \( u_0 \) and \( v_0 \) are site-exclusion interactions which assign infinite energy to any configuration in which a site is occupied by two or more segments. The partition function for a system of \( N_p \) \( n \)-mers on a lattice of \( N \) sites is

\[
Z(N_p, n, N, \beta) = \frac{1}{N_p!} \sum_{x_1^{(i)} \in A_N} \ldots \sum_{x_{N_p}^{(i)} \in A_N} e^{-\beta \sum_{i=1}^{N_p} U_{N_p}},
\]

(3.192)

where \( A_N \) is a region of the lattice encompassing \( N \) sites, and \( \beta = 1/K_B T \).

Let \( Y \) denote an \( n \)-mer configuration, and let \( X \) denote a configuration of \( N_p \) \( n \)-mers on a lattice of \( N \) sites. A quantity of key interest is the insertion factor

\[
p(N_p, n, N, \beta) = \langle e^{-\beta U_T} y \rangle_x
\]

(3.193)

where \( U_T \) is the potential energy of "test-chain" configuration \( Y \), when inserted into the main-chain configuration \( X \). The brackets indicate ensemble averages over the system and test-chain configurations. Referring to eq. (3.192), we have \( p(N_p, n, N, \beta) \)
\[
\sum_{n} \sum_{n_{p+1}} e^{-\beta U_{n_{p+1}}} = \left[ \sum_{n_{p}} \sum_{n_{a}} e^{-\beta U_{n_{p}}} \right] \left[ \sum_{n_{p}} \sum_{n_{j}} e^{-\beta U_{n_{j}}} \right] \\
= (N_{p} + 1) \frac{Z(N_{p} + 1, n, N, \beta)}{Z(N_{p}, n, N, \beta)Z(1, n, N, \beta)}
\]

The partition function may therefore be written as

\[
Z(N_{p}, n, N, \beta) = \frac{[Z(1, n, N, \beta)]^{N_{p}}}{N_{p}!} \prod_{j=1}^{N_{p}} p(i, n, N, \beta)
\]

(3.195)

Using \( \pi \) and \( \mu \) to denote, respectively, the pressure and chemical potential of the chains, we have the thermodynamic relation

\[
\mu N_{p} = E - TS + \pi N
\]

(3.196)

If we use the relations

\[
A(N_{p}, n, N, \beta) = E - TS = -k_{B}T \ln Z(N_{p}, n, N, \beta)
\]

(3.197)

and

\[
\mu(N_{p}, n, N, \beta) = -k_{B}T \left[ \ln Z(N_{p} + 1, n, N, \beta) - \ln Z(N_{p}, n, N, \beta) \right]
\]

(3.198)

together with eq. (3.195), then we have
\[
\pi^* (N_p, n, N, \beta) = N^{-1} \left[ \sum_{j=1}^{N_p-1} \ln p(j, n, N, \beta) - N_p \ln p(N_p, n, N, \beta) \right] + N_p \ln (N_p + 1) - \ln N_p \right] \tag{3.199}
\]

where \( \pi^* = \beta \pi \).

Let us assume the existence of the limiting insertion factor.

\[
p(\phi, n, \beta) = \lim_{N, N_p \to \infty, n N_p / N = \phi} p(N_p, n, N, \beta) \tag{3.200}
\]

Taking the limit \( N, N_p \to \infty \), with fixed occupation fraction \( \phi \), eq. (3.197) becomes the osmotic equation of state

\[
\pi^*(\phi, n, \beta) = \frac{\phi}{2} \left[ 1 - \ln p(\phi, n, \beta) \right] + \frac{1}{n} \int_{0}^{\phi} \ln p(\phi', n, \beta) d\phi' \tag{3.201}
\]

now for fully flexible case \( u' = v' = 0 \), i.e. athermal chains on a lattice. Since the only interactions are site-exclusion, \( e^{-\beta u} = 1 \) if the configuration is free of overlap, and is zero otherwise. Thus \( p(N_p, n, N) \) may be interpreted as the probability that a randomly chosen \( n \)-mer may be inserted without overlap into a randomly chosen configuration of \( N_p \) \( n \)-mers on a lattice of \( N \) sites. The Flory (F) and Flory-Huggins (FH) theories provide simple estimates for \( p(\phi, n) \) for athermal lattice chains.

Let \( \chi(Y, X) \) be 1 if chain \( Y \) does not overlap with any of the \( N_p \) chains in configuration \( X \), and let \( \chi \) be zero otherwise. Then the insertion probability can be expressed as an average over configurations:
\[ p(N_p, n, N) = \langle \chi(Y, X) \rangle_Y \langle \chi(Y, X) \rangle_X \]  

(3.202)

where averages overall the \( y \) and \( x \) are indicated. It is also defined by

\[ P_{N_p, n, N}(Y) = \langle \chi(Y, X) \rangle_X \]  

(3.203)

which is the probability that \( n \)-mer configuration \( Y \) may be inserted without overlap into a randomly chosen configuration of \( N_p \) \( n \)-mers, so that

\[ p(N_p, n, N) = \langle P_{N_p, n, N}(Y) \rangle_Y. \]

For \( y_i, y_j, \) etc., \( \in \Lambda_N \), define \( P_{N_p, n, N}(y_i | y_k, \ldots, y_m) \) as the probability that \( y_i \) is vacant in a randomly chosen configuration of \( N_p \) \( n \)-mers on a lattice of \( N \) sites, given that sites \( y_k, \ldots, y_m \) are vacant. Let \( Y = (y_1, y_2, \ldots, y_n) \), where the sites are listed in their order along the chain. Then

\[ P_{N_p, n, N}(Y) = (1 - \phi) P_{N_p, n, N}(y_2 | y_1) P_{N_p, n, N}(y_3 | y_1 y_2) \]

\[ \times \cdots \times P_{N_p, n, N}(y_n / y_1, \ldots, y_{n-1}) \]  

(3.204)

In the Flory approximation sites \( y_1, \ldots, y_n \) are regarded as occupied independently with probability \( \phi \), so that \( k \geq 2 \),

\[ P_{N_p, n, N}(y_k | y_1, \ldots, y_{k-1}) = (1 - \phi) \]  

(3.205)

which immediately yields

\[ P_F(\phi, n) = (1 - \phi)^n \]  

(3.206)
The Flory approximation treats the occupied sites as if they were scattered randomly over the lattice, rather than grouped in chains.

To derive the FH formula for \( p \), we first invoke a Markovian assumption

\[
P_{N_p,n,N}(y_k|y_1,\ldots,y_{k-1}) = P_{N_p,n,N}(y_k|y_{k-1})
\]

(3.207)

for \( k \geq 2 \). As a result of this approximation, the insertion probability

\[
P_{N_p,n,N}(Y) = (1-\phi)^n P_{N_p,n,N}(y|y')^{n-1}
\]

(3.208)

is independent of \( Y \), since \( y \) and \( y' \) are an arbitrary pair of neighbouring sites.

Thus \( p_{nh}(n_p,n,N) = (1-\phi)(1-\phi_o)^{n-1} \), where \( \phi_o \) is the probability that a neighbor of a randomly chosen vacant site is occupied. While this represents a considerable simplification over eq. (3.204) determination of \( \phi_o \) is not trivial, since knowledge of the pair correlation for vacant sites is required. In the FH theory \( \phi_o \) is approximated as the occupation probability \( \bar{\phi} \) of a neighbor of any site (occupied or vacant), excluding pairs of sites occupied by successive segments of a chain. The accuracy of this approximation is difficult to assess, but it clearly represents an improvement over the complete disregard for chain structure inherent in the Flory approximation \( \bar{\phi} \) may be evaluated as follows.

If a fraction \( \phi \) of the sites are occupied by chain segments, then \( N\phi(n-2)/n \) sites are internal to chains. Denoting the lattice coordination number by \( z \), the density of occupied neighbours of the internal sites is
\[
\phi_{\text{in}} = \frac{z - 2}{z} \phi + \frac{2}{z}, \quad (3.209)
\]

since each internal site has two neighbours which are surely occupied. Similarly, neighbours of the 2N\phi/n chain-end sites are occupied with probability

\[
\phi_{\text{end}} = \frac{z - 1}{z} \phi + \frac{1}{z}, \quad (3.210)
\]

and, by assumption, neighbours of the N(1-\phi) vacant sites are occupied with probability \( \tilde{\phi} \). Since the overall fraction of occupied sites is \( \phi \), we must have

\[
\phi = \phi \left[ \left( 1 - \frac{2}{n} \right) \phi_{\text{in}} + \frac{2}{n} \phi_{\text{end}} \right] + (1 - \phi) \tilde{\phi}, \quad (3.211)
\]

which implies that

\[
\tilde{\phi} = \phi \frac{1 - 2z^{-1}(1 - n^{-1})}{1 - 2\phi z^{-1}(1 - n^{-1})} \quad (3.212)
\]

The insertion probability in the FH approximation is therefore

\[
p_{\text{FH}}(\phi, n) = (1 - \phi) \left( 1 - \tilde{\phi} \right)^{n-1} = (1 - \phi)^n \left[ 1 - 2\phi z^{-1}(1 - n^{-1}) \right]^{(n-1)} \quad (3.213)
\]

Numerical studies [91-97] indicate that at low and moderate densities the F and FH formulas tend to underestimate the insertion probability. However, the FH estimate for the pressure is quite accurate over a wide range
of densities. The disparity between F and FH predictions and numerical results worsens with increasing chain length, which is not surprising, given that (1) and F and FH theories are exact for \( n = 1 \), and (2) correlations within and between chains (ignored in these theories) assume greater importance for longer chains.

(c) **Extension to Off-Lattice Models**

F and FH approximations, originally derived for lattice models, are frequently applied to off-lattice models. It is rather easy to extend the F and FH approaches to a continuous space context, and to derive expressions analogous to eqs. (3.206) and (3.213), which provide accurate predictions for the pressure in a system of athermal chains.

Let \( Z(N_p, n, V, \beta) \) be partition function for a system of \( N_p \) \( n \)-mers in volume \( V \), and let \( p(N_p, n, V, \beta) \) be the insertion factor, i.e., eq. (3.193) with \( N \) replaced by \( V \). The relation between \( p \) and \( Z \) is again given by eq. (3.194), if we replace \( N \) by \( V \). In analogy with eq. (3.200), we assume the existence of

\[
p(\eta, n, \beta) \equiv \lim_{N_p \to \infty; N_p \nu_n / V = \eta} P(N_p, n, V, \beta)
\]  
(3.214)

where \( \nu_n \) is the volume of an \( n \)-mer. If \( N \) is represented by \( V \), eq. (3.199) also holds for continuous space systems, and in the thermodynamic limit the continuous space version of the osmotic equation of state is

\[
\pi^*(\eta, n, \beta) = \frac{\eta}{\nu_n} \left[ 1 - \ln p(\eta, n, \beta) \right] + \frac{1}{\nu_n} \int_{0}^{\eta} \ln p(\eta', n, \beta) d\eta'
\]  
(3.215)
Comparing this with eq. (3.201), one may be tempted to conclude that
the continuous space system is described by the lattice formula, with \( \phi \to \eta \)
and \( n \to \nu_n \). However, it will be seen presently that \( p_{\text{continuum}}(\eta) \neq p_{\text{lattice}}(\eta) \).
In fact, the dependence of the insertion probabilities on the volume fraction is
radically different in the two cases.

To begin Dickman Hall consider the case of athermal chains with \( n = 1 \), for which the lattice F and FH theories both give \( p(\phi, 1) = (1 - \phi) \), which is
exact. In this case, eq. (3.199) yields the familiar result

\[
\pi^* (\phi, 1) = -\ln(1 - \phi)
\]  

(3.216)

For arbitrary \( n \), the Flory approximation predicts the compressibility factor

\[
\rho_n^{-1} \pi^* (\phi, n) = 1 - \frac{n}{\phi} \left[ \ln(1 - \phi) + \phi \right]
\]

(3.217)

where \( \rho_n \) is the number of chains per unit volume. Equation (3.217) (with \( \phi \)
replaced by \( \eta \)) is commonly cited as the Flory theory prediction for the
compressibility factor in a system of athermal chains in continuous space.
Since, on the lattice, the F and FH theories are exact for \( n = 1 \) and only
approximate for \( n > 1 \), we should not expect eq. (3.217) to be a good
approximation for the continuum unless the pressure in a system of monomers
(e.g., hard spheres) is well approximate by \( -\ln (1 - \eta) \). But this is obviously a
gross underestimate of the pressure. For example, the pressure in the fluid
phase of hard spheres is accurately described by the Carnahan-Starling
equation [62].

\[ \pi_{CS}(\eta) = \rho \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \]  \hspace{1cm} (3.218)

while in the case of hard rods of length \( \sigma \) on a line, we have the exact result [98].

\[ \pi_{rods}(\eta) = \frac{\rho}{1 - \eta} \]  \hspace{1cm} (3.219)

where \( \eta = \sigma \rho \). We see that as the volume fraction approaches unity, the pressure increases much more rapidly in continuous-space models than on the lattice. (The same conclusion applies to the FH lattice approximation, which predicts a compressibility factor somewhat smaller than in the F approximation).

In order to derive generalization of the F and FH theories for athermal chains in continuous space, consider the monomer insertion probability \( p(\phi, 1) = -(1-\phi) \), for a continuous space model. From equation (3.215), we have

\[ \ln p(\eta, 1) = \int_{0}^{\eta} \frac{d\eta'}{\eta'} \left[ 1 - \nu_1 \frac{d\pi^*(\eta', 1)}{d\eta'} \right] \]  \hspace{1cm} (3.220)

The monomer insertion probability for hard spheres, derived from the Carnahan-Starling equation (3.218), is readily found to be

\[ p_{CS}(\eta, 1) = \exp \left[ -\frac{\eta(8 - 9\eta + 3\eta^2)}{(1 - \eta)^3} \right] \]  \hspace{1cm} (3.221)
Which again decays rapidly with increasing $\eta$.

In a fluid composed of hard sphere molecules (monomers) of diameter $\sigma$, if a molecule is centered at $x$, then no other monomers may have their centers within the sphere of radius $\sigma$, centered at $x$. The exclusion volume associated with a monomer is $v_e(1) = \frac{4\pi\sigma^3}{3}$, and $p(\eta, 1)$ is the probability that a sphere of volume $v_e(1)$, inserted at random into a fluid of hard-sphere $n$-mers is free of centers of any chain segments, i.e., $p_t(\eta, n)$ is the probability for insertion of a single spherical segment into the $n$-mer fluid. We shall approximate $p_t(\eta, n)$ by $p_t(\eta, 1)$, the insertion probability for the monomer fluid. With each $n$-mer configuration $Y$ we may associate an exclusion region: the region of space which must be free of centers of monomers, if insertion of $Y$ is possible. The insertion probability $P(Y)$ is the probability of finding the corresponding exclusion region, centered at a randomly chosen point in the fluid, free of centers of monomers. Clearly, an exact evaluation of $P(Y)$ would require knowledge of the probability distribution for voids in the fluid. In the absence of detailed information regarding the distribution of voids, we shall assume that $P(Y)$ is a function of the exclusion volume $v_e(Y)$ only. As in the Flory lattice argument, we shall also assume that the vacancies of disjoint regions constitute independent events. Under these assumptions, the insertion probability becomes

$$P_F(Y) = [p(\eta, 1)]^{v_e(Y)} v_e(1)$$  \hspace{1cm} (3.222)

and therefore,
\[ P_F(\eta, n) = [p(\eta, 1)]^{\nu_e(n)} \nu_e(1) \] (3.223)

where \( \nu_e(n) \) is the \( n \)-mer exclusion volume, and the subscript \( F \) denotes the extension of the Flory-type argument to continuous space.

It is important to note that in general \( \nu_e(n) \neq n\nu_e(1) \). For example, in the case of hard spheres, the overlap between exclusion regions associated with neighbouring monomers is such that

\[ \nu_e(2) = \frac{9}{4} \pi \sigma^3 = \frac{27}{16} \nu_e(1). \] (3.224)

For \( n \geq 3 \), \( \nu_e(Y) \) may depend on the particular choice of \( Y \); \( \nu_e(n) \) is then the exclusion volume averaged over all \( n \)-mer configurations.

Inserting eq. (3.223) into the equation of state, eq. (3.215), we find

\[ \pi_0^* (\eta, n) = \frac{\eta}{\nu_n} \left[ 1 - \frac{\nu_e(n)}{\nu_e(1)} \ln p(\eta, 1) \right] \]
\[ + \frac{\nu_e(n)}{\nu_e(1)\nu_n} \int_{\eta'}^{\eta} \ln p(\eta', 1) d\eta' \]
\[ = \lambda_n \pi_0^* (\eta, 1) + \rho_n \left( 1 - \frac{\nu_e \lambda}{\nu_1} \right) \] (3.225)

where \( \lambda_n = \nu_1 \nu_e(n)/\nu_n\nu_e(1) \). Equations (3.223) and (3.225) constitute the extension of Flory theory to a continuous space system of athermal chains.

The generalization of the FH approach to continuous space models is based on the idea that the volume fraction \( \bar{\eta} \) in the neighbourhood of a void
large enough to accommodate a monomer, is smaller than the average volume fraction \( \eta \), because monomers are grouped together in chains. Thus the FH estimate for the insertion probability is

\[
p_{FH}(\eta, n) = p(\eta, 1)[p(\bar{\eta}, 1)]^{\nu_e(n)/\nu_e(1)-1}
\]  

(3.226)

In deriving \( \bar{\eta} \) for continuous space models, the chain of reasoning employed in eqs. (3.307-3.213), being followed the sole modification being that the lattice coordination number \( z \) is replaced by \( \bar{z} \), the average coordination number at close packing. Since we are considering a disordered phase, the coordination number characteristics of random close packing is appropriate \( \bar{z} = 9 \) for hard spheres, [99] and \( \bar{z} = 5 \) for hard disc [100]. By analogy with eq. (3.212).

\[
\bar{\eta} = \eta \frac{1 - 2\bar{z}^{-1}(1 - n^{-1})}{1 - 2\eta\bar{z}^{-1}(1 - n^{-1})} = \frac{\eta(1 - \alpha)}{1 - \alpha\eta},
\]  

(3.227)

where \( \alpha = 2\bar{z}^{-1}(1 - n^{-1}) \)

The organisation of the FH approximation to continuous space systems yields the equation of state

\[
\pi_{FH}^*(\eta, n) = \frac{\nu_l}{\nu_n} \pi^*(\eta, 1) - \left( \frac{\lambda_n}{\nu_l} - \frac{1}{\nu_n} \right)
\]

\[
x \left[ \eta \ln p(\bar{\eta}, 1) - \int_0^n \ln p(\eta', 1) d\eta' \right]
\]  

(3.228)
where $\tilde{\eta}$ is given by eq. (3.227) with $\eta'$ in place of $\eta$. Using eq. (3.227) and integrating the last term by parts, one finds,

$$
\pi_{FH}^*(\eta, n) = \frac{\nu_l}{\nu_n} \pi^*(\eta, l) - \left( \frac{\lambda_n}{\nu_l} - \frac{1}{\nu_n} \right) \int^n_0 \frac{d\eta'}{1 - \alpha \eta'} \left[ 1 - \nu_l \frac{d\pi^*(y; 1)}{dy} \bigg|_{y = (1 - \alpha) \eta' / (1 - \eta')} \right]
$$

for the pressure in the generalized FH approximation. If $\pi^*(\eta, 1)$ taken to be the Carnahan Starling equation (3.218) the above expression yields

$$
\pi_{FH-CS}^*(\eta, n) = n^{-1} \pi_{CS}^*(\eta, l) + \nu_n^{-1} \left( \frac{\nu_e(n)}{\nu_e(l)} - 1 \right) (1 - \alpha) X \left( 2\alpha(1 + 3\alpha) \ln(1 - \eta) + \frac{\eta}{(1 - \eta)^3} \right)
$$

$$
X \{ 2\alpha(1 + 3\alpha) + [4 - 5\alpha(1 + 3\alpha)] \eta 
$$

$$
- \left( 2 + \alpha - 11\alpha^2 \right) \eta^2 \right) \} \right)
$$

(3.230)

The generalized F and FH theories will be compared against other theories and simulation results in the following section.

While (3.225) and (3.229) have been derived for athermal models, the following argument suggests that they are valid for more general interactions. Consider models in which the intermolecular potential $u$ includes a steep repulsion (e.g., hard-core square-well or Lennard-Jones potentials), with which a hard-core diameter $\sigma_0$ may be associated. Then we may take
\[ \nu_l = \frac{\pi \sigma_0^3}{6} \text{ and } \eta = n \rho n \nu_l, \] so that the parameters in eq. (3.229) are well defined. [Of course, \( \pi^* (\eta, n, \beta) \) is now the pressure in a monoatomic system with interparticle potential \( u \). For those configurations which make the dominant contribution to \( p(\eta, n, \beta) \) (i.e., those for which \( U_T \) is small), the presence of a test-chain segment effectively excludes segments of other chains from a sphere of radius \( \sigma_0 \). The argument based on the overlap of exclusion regions of successive segments along a chain therefore remains valid, and so eqs. (3.225) and (3.229) to be applicable to nonathermal models with an effective hard core.

### 3.7.2 GENERALISED FLORY THEORY

In the Flory [101] F and Flory-Huggins [102] (FH) theories the configurational space description of the chains is simplified by restricting the molecules to lie at discrete points on a lattice. The system is then characterized by specifying the number of sites (monomers) per chains \( n \) and the occupation fraction of \( \phi \) which is the fraction of lattice position occupied by chains. For convenience, we let \( p^*(\phi, n) = p(\phi, n, t)/kT \). Where \( p(\phi, n, t) \) is the pressure of a \( n \)-mer fluid at occupation fraction of \( \phi \) and \( kT \) is the product of Boltzmann's constant and the temperature.

The starting point for the derivation of the F and FH equations is the "osmotic equation of state" [85].

\[
p^*(\phi, n) = \frac{\phi}{n} \left[ 1 - \ln p_n (\phi) \right] + \frac{1}{n} \int_0^\phi \ln p_n (\phi') d\phi'
\] (3.231)
which relates the pressure to the insertion probability \( p_n(\phi) \), defined to be the probability of inserting a randomly chosen \( n \)-mer into a random configuration of \( n \)-mers at occupation fraction \( \phi \) without creating an overlap equation (3.231) is exact in the macroscopic limit, so the problem of obtaining accurate equation of state is reduced to developing reasonable estimates for the chain insertion probability. Equation (3.231) is also valid for systems with attractive or many body interaction, though \( p_n \) becomes function of both \( T \) and \( \phi \) and can non longer be interpreted as the probability of inserting a chain without creating an overlap [85].

The term osmotic in reference to eq. (3.231) derives from the fact that the lattice fluid may be viewed in two different ways. If one considers all of the lattice sites to be occupied a fraction \( \phi \) by chains and a fraction \( (1-\phi) \) by monomers then eq. (3.231) gives the osmotic pressure of the solution. Alternatively, if only the chains are present and the monomer sites are vacant, eq. (3.231) yields the thermodynamic pressure of the pure chain fluid. For off-lattice fluids, the continuous-space analog of eq. (3.231) gives only the thermodynamic pressure, though, it is referred to as the osmotic equation of state.

In general, the probability of inserting a chain into a chain fluid without creating an overlap is a difficult quantity to estimate. Conceptually, however, the process is simplified by managing that the chain is inserted one site at a time. On the lattice, the probability of inserting the first site is given exactly by \( (1-\phi) \), since that is the chance of picking an empty site at random. The probability of inserting the second and successive sites will be different, though, due to the influence of neighboring chains and intramolecular correlations on the local structure of the fluid.
In the Flory theory, these effects are ignored, and \((1-\phi)\) is taken as the estimate for the insertion probability of each of the \(n\) sites. The Flory estimates for the chain insertion probability is then

\[
p_n^F(\phi) = (1-\phi)^n
\]  

(3.232)

The net effect of the Flory approximation is to treat the \(n\) sites as if they were inserted at random throughout the fluid, rather than being grouped together in a connected chain. Thus, the Flory ignores the detailed structure of the fluid and treats the system in an average, or mean-field, sense.

In reality, the probability of successfully inserting the \(i^{th}\) site of a chain is somewhat greater than that for the first site, since the fact that \(i-1\) sites have previously been inserted means that a neighboring molecule is less likely to be found nearby. Thus, the Flory theory tends to underestimate the chain insertion probability. The Flory-Huggins theory tries to account for this effect by adding in a correction term to eq. (3.232) which, in an approximate way, incorporates the effects of chain connectivity [85].

Substitution of eq. (3.232) into eq. (3.321) leads to the Flory equation of state

\[
Z^F(\phi, n) = 1 - \frac{n}{\phi} \left[ \ln(1-\phi) + \phi \right]
\]  

(3.233)

where \(Z(\phi, n)\) is the compressibility factor, \(Z(\phi, n) = p^*(\phi, n)/\rho_n\), and \(\rho_n\) is the number density of chains, \(\rho_n = \phi/n\). A similar, though somewhat more complicated, expression can be obtained from the Flory-Huggins theory [101, 102]. Unlike the F
equation, the FH expression depends explicitly on the lattice coordination number.

Comparisons with Monte Carlo results for athermal lattice chains show that the F and FH equations give reasonably accurate predictions for the compressibility factor, particularly at intermediate and high densities where chain interpenetration increases the accuracy of the mean-field approximations [93, 103]. The Flory equation tends to overestimate the pressure over the entire density range, while the Flory-Huggins equation goes from overestimating the pressure at low densities to underestimating it at higher densities. As might be expected from the neglect of intra and intermolecular correlations, the agreement generally worsens with increasing chain length.

Though originally derived for lattice fluids, the F and FH theories have often been applied to continuous space systems. Generally, this is accomplished by replacing the occupation fraction \( \phi \) appearing in eq. (3.233) by the volume fraction \( \eta \), and, for the FH model, associating the lattice coordination number with the average number of nearest neighbors at close packing [85]. The volume fraction is defined as the volume of space occupied by the chains, divided by the total volume of the system,

\[
\eta = \frac{n \pi \sigma^3}{6 \rho_n}
\]  \hspace{1cm} (3.234)

where \( \rho_n \) is the number density of n-mers, \( \rho_n = N/V \). Comparisons with simulation results for off-lattice chains, however, show that the traditional F and FH theories severely underestimate the pressure of continuous space fluids [85, 103, 104].
Fig. 3.4: Approximations involved in the GF and GF-D theories: (a) In the GF theory, the probability of inserting a monomer (denoted by shaded circle) into a chain fluid is approximated by the probability of inserting a monomer into a monomer fluid at the same volume fraction, $P_1(\eta)$; (b) In addition, in the GF-D theory the probability of inserting a dimer into a chain fluid is approximated by the probability inserting a dimer into a dimer fluid, $P_2(\eta)$. Physical arguments suggest that the second approximation will be more accurate than the first.

The starting point for the derivation of the Generalized Flory (GF) equation is the continuous space version of the osmotic equation of state [85].

$$P^*(\eta, n) = \frac{\eta}{\nu_n} \left[1 - \ln p_n(\eta)\right] + \frac{1}{\nu_n} \int_0^\eta \ln p_n(\eta') d\eta'$$  \hspace{1cm} (3.235)

Here $\nu_n$ is the volume occupied by a $n$-mer ($\nu_n = n\pi\sigma^3/6$), and $p_n(\eta)$ is the continuous space chain insertion probability. Reviewing for a moment, the Flory estimate for the insertion probability eq. (3.232) consisted of two parts: a base factor of $(1 - \phi)$, which was the probability of inserting a monomer; and an exponent $n$ which was the number of monomers being inserted. In extending this expression to off-lattice fluids, Dickman and Hall replaced each of these quantities by their continuous space
analogs. The continuous space analog of the base is the probability of inserting a monomer into a continuous space chain fluid. Since this is, in general, a complicated and unknown quantity, they approximated the probability of inserting a monomer into a chain fluid by \( p_1(\eta) \), the probability of inserting a monomer into a monomer fluid at the same volume fraction (see fig. 3.4). The physical motivation behind this approximation is that at intermediate and high densities, where there is significant chain-chain interpenetration, an individual chain segment finds itself surrounded on all sides by other chain segments. Thus, as the density is increased, it becomes increasing difficult for a monomer to distinguish between neighbors that are numbers of the same chain and neighbors that are not, so, to a first approximation, the structure of a chain fluid can be modeled by the structure of a simple hard sphere fluid. These, of course, are the same physical arguments underlying the Flory and Flory-Huggines lattice theories [85, 101, 102] as well as Croxton's screened convolution approximation [105]. At low densities, though, the approximation will begin to break down, since in regions where a chain is located the local density will be much higher than average and in regions between chains the local density will be much lower. Under these circumstances, the "patchy" local density of the chain fluid does not resemble the uniform density of a monomer fluid at the same volume fraction. Consequently, at low densities this approximation leads to underestimates for the chain insertion probability and, hence, overestimates for the pressure. Accordingly, the GF, and GFH theories tend to overestimate the second virial coefficient just as the F and FH theories overestimate the lattice based second virial coefficient [93, 106].
The second step in the transcription from lattice to continuous space deals with the exponent $n$ appearing in eq. (3.232). Upon first consideration, it seems as though the factors should be retained as the exponent in the generalized theory since, after all, $n$ monomer sites are being inserted. However, a closer inspection suggests that the continuous space exponent should be somewhat smaller. To see this, it is useful to consider the factor $n$ in eq. (3.232) not as the number of sites per chain, but, rather, as the ratio of the amount of space occupied by the chain to the amount of space occupied by a monomer. In developing this idea for continuous space fluids, Dickman and Hall [85] made use of the concept of an "exclusion volume", which characterizes the size of the hole needed in the fluid to successfully insert the n-mer. The exclusion volume of an n-mer, $\nu_e(n)$, is defined as the amount of space excluded by the chain to the centers of sites on other molecules. It is not difficult to show that $\nu_e(n)$ is just the crossed second virial coefficient of a chain-monomer mixture, i.e., the coefficient of the $\rho_1 \rho_n$ term in the virial expansion for the pressure.

![Diagram](image)

**Fig. 3.5:** Use of exclusion volumes to estimate the insertion probability of a dimer. The two hard sites of diameter $\sigma$ are denoted by solid circles and the associated exclusion volumes, which must be free of the centres of other sites in order to avoid an overlap, are denoted by the dashed curves. Insertion of the first site requires a hole in the fluid (an exclusion volume) of volume $4\pi \sigma^3/3$. The second site requires a smaller hole in the fluid (represented by the shaded region) and, hence, will be easier to insert.
Dickman and Hall used the monomer and n-mer exclusion volumes to develop a continuous-space analog of the exponent \( n \). These ideas are illustrated for a dimer fluid in fig. 3.5. The two solid circles represent the hard-sphere sites of diameter \( \sigma \); the dashed curves denote the associated exclusion volumes of radius \( \sigma \). The GF estimate for the probability of inserting the first site is \( p_1(\eta) \). Insertion of the first site requires a hole in the fluid, which is free of the centers of neighboring sites, of volume \( 4\pi\sigma^3/3 \). Thus the exclusion volume of the first site is \( \nu_e(1) = 4\pi\sigma^3/3 \). In that this is the amount of space required by one monomer, \( \nu_e(1) \) becomes the continuous space analog of one lattice site. The second site, however, will require a smaller hole in the fluid (denoted by the shaded region in fig. 3.5), by virtue of being next to site 1, and, hence, will be easier to insert. The relative ease of inserting the second site compared to the first can be gauged by comparing the size of the cavity required to insert the second site to the size of the cavity required to insert the first site. Letting \( \nu_e(2) \) denote the exclusion volume of the dimer (that is, the cavity required by both sites), the ratio of the volume required by the second site to that required by the first is given by \( [\nu_e(2) - \nu_e(1)]/\nu_e(1) \) which is less than one.

Combining these ideas, the GF estimate for the conditional probability of adding on the second site, given that the first has been successfully inserted, becomes.

\[
p_1(\eta)[\nu_e(1)] [\nu_e(1)] [\nu_e(1)] (3.236)
\]

In this fashion one can build up a chain of \( n \) sites by continuing to insert additional monomers, each time comparing the size cavity required for the new site
to the size of the cavity required for the first site. The GF estimate for insertion probability of the entire chain is then the product of the individual insertion probabilities for each of the n sites,

\[ p_n^{\text{GF}}(\eta) = p_1(\eta)^{\nu_e(n)/\nu_e(1)} \]  

(3.237)

Notice that in the lattice fluid each chain site occupies the same amount of space-namely, one lattice site. Thus, on the lattice \( \nu_e(n) = n \nu_e(1) \), and the GF exponent reduces to the F exponent \( n \).

Substitution of eq. (3.237) into (3.235) leads to the GF equation of state [85]

\[ Z_n^{\text{GF}}(\eta) = \frac{\lambda_n \nu_n}{\nu_1} Z_1(\eta) + 1 - \frac{\lambda_n \nu_n}{\nu_1} \]  

(3.238)

which relates the compressibility factor of a n-mer fluid to the compressibility factor of a monomer fluid at the same volume fraction. Here, \( \nu_n \) denotes the volume of a n-mer and \( \lambda_n \) is a parameter which depends on the monomer and chain exclusion volumes through the relation \( \lambda_n = \nu_1 \nu_e(n)/[\nu_n \nu_e(1)] \). The generalized Flory-Huggins (GFH) equation of state can be derived by following a similar procedure using the more sophisticated GFH estimate for the chain insertion probability [85]. In evaluating eq. (3.138), Dickman and Hall used the Carnahan-Starling equation of state of monomers [62].

The values employed for the exclusion volumes will depend upon the particular molecular model being studied. For the freely jointed hard chain, \( \nu_e(n) \) is obtained by Averaging over all possible configurations of an isolated n-mer. For
short chains, the exclusion volumes can be evaluated from geometrical considerations using the formulas derived by Lustig [107] for the volumes of overlapping hard spheres. The exclusion volumes for $n = 1, 2$ and $3$ are

$$v_e(1) = \frac{4}{3} \pi \sigma^3,$$

$$v_e(2) = \frac{9}{4} \pi \sigma^3,$$

$$v_e(3) \approx 9.82605 \sigma^3.$$  \hspace{1cm} (3.239)

For $n \geq 4$ the exact evaluation of $v_e(n)$ becomes an increasingly difficult task; however, it can be estimated from [85]

$$v_e \approx v_e(3) + (n-3)[v_e(3)-v_e(2)]$$  \hspace{1cm} (3.240)

Comparisons of the GF and GFH equations to Monte Carlo results for the compressibility factor of two and three dimensional chains have shown relatively good agreement [85, 104]. The GF equation tends to overestimate the pressure, while the more accurate GHF equation goes from overestimating the pressure at low densities to underestimating it at higher densities.

### 3.7.3 Generalized Flory-Dimer (GF-D) Theory

In order to develop a new equation of state for athermal chain which is to be referred as the Generalized Flory-Dimer (GF-D) equation. Let us consider two approximations relating the chain fluid to monomer & dimer reference fluids. The probability of inserting a monomer into a chain fluid is approximated by the probability of inserting a monomer into a monomer fluid.
Within the context of these approximations, since \( p_1(\eta) \) is the probability of inserting a monomer and \( p_2(\eta) \) is the probability of inserting a dimer, the ratio \( p_2(\eta)/p_1(\eta) \) is the conditional probability of adding a second site next to one already present in the fluid. This ratio then provides a way of building up longer chains by tacking on additional sites, one at a time. The general procedure is illustrated in fig. 3.6. Again, the circles denote the hard-sphere sites while the larger dashed curves represent the associated exclusion volumes. The quantities on the right-hand side are the new estimates for the conditional probability of adding in the last site, given that the previous sites have been successfully inserted. The probability of inserting the first site is the same as in the GF theory, \( p_1(\eta) \). The new estimate for the probability of inserting the second site is \( p_2(\eta)/p_1(\eta) \), which can be compared with the GF estimate of \( p_1(\eta)[v_2-\nu_1]/v_1 \). The situation becomes more complicated when we turn to the third site, since its insertion probability is unknown. It seems reasonable to expect, though, that the probability of adding the third site to the second is approximately equal to the probability of adding the second site to the first, and we can try to correct for the difference between the two by comparing the size of the hole (exclusion volume) required to insert the third site (denoted by the horizontally shaded region in fig. 3.6) to that required to insert the second site (denoted by the crossed-hatched region in fig. 3.6). If the third site requires a longer hole than the second site, then one expects that it will be proportionally harder to insert, and conversely, if the third site requires a smaller hole than its predecessor, it should be proportionally easier to insert. Since the ratio of these two exclusion volumes is given by
Conditional prob. of adding site I

\[ i = 1 \]

\[ \begin{pmatrix} \frac{p_2}{p_1} \\ \frac{p_3}{p_1} \end{pmatrix} \]

\[ i = 2 \]

\[ \begin{pmatrix} \frac{p_2}{p_1} \\ \frac{p_3}{p_1} \end{pmatrix} \]

\[ \frac{v_e(3) - v_e(2)}{v_e(2) - v_e(1)} \]

\[ i = 3 \]

\[ \begin{pmatrix} \frac{p_2}{p_1} \\ \frac{p_3}{p_1} \end{pmatrix} \]

\[ \frac{v_e(4) - v_e(3)}{v_e(2) - v_e(1)} \]

\[ i = 4 \]

\[ \begin{pmatrix} \frac{p_2}{p_1} \\ \frac{p_3}{p_1} \end{pmatrix} \]

\[ \frac{v_e(4) - v_e(3)}{v_e(2) - v_e(1)} \]

Fig. 3.6: Development of the GF-D estimate for the chain insertion probability. A chain is inserted one site at a time. The solid circles represent the hard sites and dashed curves are the associated exclusion volumes. The value of \( i \) denotes the site being inserted. Numerical quantities on the right are the GF-D estimates for the conditional probability of adding site \( i \), given that the previous \( i-1 \) sites have been successfully inserted. For \( i>3 \) the probability of inserting site \( i \) is related to the probability of inserting site 2 by comparing the size of the hole (exclusion volume) required by site \( i \) (denoted by the horizontally shaded region) to the size of the hole required by site 2 (denoted by the cross-hatched region). The ratio of these two exclusion volumes appears as the exponent in the GF-D estimate for the conditional probability of inserting site \( i \). The insertion probability of the entire chain is the product of the conditional probabilities for each site.
\[
\frac{\nu_e(3) - \nu_e(2)}{\nu_e(2) - \nu_e(1)}
\]  
(3.241)

the GF-D estimate for the conditional probability of adding in the third site becomes

\[
\begin{pmatrix}
\frac{p_2(\eta)}{p_1(\eta)}
\end{pmatrix}^{[\nu_e(3) - \nu_e(2)]/[\nu_e(2) - \nu_e(1)]}
\]  
(3.242)

Similarly, the probability of inserting the fourth site can be estimated by comparing the size of the hole it will require (again represented by the horizontally shaded region in fig. 3.6) to the size of the hole required by site 2 (represented by the cross-hatched region in fig. 3.6). Proceeding in this fashion, each of the \( n \) sites may be inserted.

The probability of inserting the entire chain is then given by the product of the individual site insertion probabilities,

\[
p_n(\eta) = p_1(\eta) \left( \frac{p_2(\eta)}{p_1(\eta)} \right)^{[\nu_e(3) - \nu_e(2)]/[\nu_e(2) - \nu_e(1)]} \times \ldots \times \left( \frac{p_2(\eta)}{p_1(\eta)} \right)^{[\nu_e(n) - \nu_e(n-1)]/[\nu_e(2) - \nu_e(1)]}
\]

\[
= p_1(\eta) \left( \frac{p_2(\eta)}{p_1(\eta)} \right)^{[\nu_e(n) - \nu_e(1)]/[\nu_e(2) - \nu_e(1)]}
\]  
(3.243)

One can gain insight into how this improves upon the GF estimate by comparing eq. (3.243) to eq. (3.237). In the GF theory, the basic building block of a chain is the monomer. Accordingly, the probability of inserting the chain is estimated from the probability of inserting a monomer, raised to a power which describes the
effective number of monomer which are to be inserted. In the new equation, the basic building block becomes the conditional probability of tacking an additional site on to one already present in the fluid. As a result, the improved estimate for $p_n(\eta)$ is equal to the product of the probability of inserting the first site and the conditional probability of adding on a new site raised to a power which describes the effective number of new sites which must be added.

For convenience, let

$$Y_n = \frac{\nu_e(n) - \nu_e(2)}{\nu_e(2) - \nu_e(1)}$$

(3.244)

Equation (3.243) can then be written more compactly as

$$P_n(\eta) = P_1(\eta)^{-Y_n} P_2(\eta)^{Y_n+1}.$$  

(3.245)

Substitution of eq. (3.245) into eq. (3.235) then gives

$$
\begin{align*}
P^*(\eta, n) &= \frac{\eta}{\nu_n} \left[ 1 + Y_n \ln P_1(\eta) \right] - \frac{Y_n}{\nu_n} \int_0^\eta \ln P_1(\eta') d\eta' \\
&\quad - \frac{\eta}{\nu_n} (Y_n + 1) \ln P_2(\eta) \\
&\quad + \frac{(Y_n + 1)}{\nu_n} \int_0^\eta \ln P_2(\eta') d\eta'.
\end{align*}
$$

(3.246)

By comparing eq. (3.246) to eq. (3.235) evaluated for $n = 1$ and $n = 2$, the monomer and dimer insertion probabilities may be eliminated in favor of the monomer and dimer pressures. One then obtains
\[ P^*(\eta, n) = \frac{u_2}{u_n} (Y_n + 1) P^*(\eta, 2) - \frac{u_1}{u_n} Y_n P^*(\eta, 1) \]  
(3.247)

in which the chain, monomer, and dimer pressures are all evaluated at the same volume fraction. This result may be expressed more compactly in terms of the chain, monomer, and dimer compressibility factors, obtained by dividing both sides of eq. (3.247) by \( \rho_n \). Since, at a given volume fraction \( \eta \),

\[ \rho_n = \frac{u_1}{u_n} \rho_1 = \frac{u_2}{u_n} \rho_2 \]  
(3.248)

we obtain

\[ Z^{\text{GF-D}}(\eta, n) = (Y_n + 1) Z(\eta, 2) - Y_n Z(\eta, 1) \]  
(3.249)

Equation (3.249) is the new equation of state referred to in the title, in which the compressibility factor of the chain is related to the compressibility factors of monomer and dimer fluids at the same volume fraction and to the ratio of exclusion volumes \( Y_n \), given by eq. (3.244)

In implementing the GF-D equation, we have used the Carnahan-Starling equation of state for monomers [62]

\[ Z(\eta, 1) = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \]  
(3.250)

and the Tildesley – Streett equation of state for dimers [40]
\[ Z(\eta_2) = \frac{1 + 2.45696\eta + 4.10386\eta^2 - 3.75503\eta^3}{(1 - \eta)^3} \]  

(3.251)

The coefficients in eq. (3.251) were determined by fitting the general functional form of the expression to Monte Carlo results for dimers. While a number of more theoretically based equations of state for hard dimers have been developed in the literature, (44, 60, 108-111) eq. (3.251) appears to be the most accurate, and thus, should allow the most accurate assessment of the approximations. In addition, Tildesley and streett have parameterized GF-D equation as a function of the bond-length-to-hard-sphere-diameter ratio \( l/\sigma \), so their equation can also be used to study chain models with other \( l/\sigma \) values.

3.8 REFERENCES


[40]. Tildesley, D.J. and Streett, W.B.; Mol. Phys. 41, 85 (1980).


[51]. (a) Kihara, T.; Rev. Mod. Phys. 25, 831 (1953).

(b) Kihara, T.; Rev. Mod. Phys. 27, 412 (1953).


