

## Statistical fluid theory for associating fluids containing alternating heteronuclear chain molecules

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**Abstract.** Statistical associating fluid theory of homonuclear dimerized chain fluids and homonuclear monomer–dimer mixture chain fluids are extended to fluids containing alternating heteronuclear chain molecules separately. The proposed models account for the appropriate site–site correlation functions at contact. The modified equations of state show a good agreement with generalized Flory dimer theory and MD simulation data for small and medium size ratio of hard sphere diameters.

**Keywords.** Heteronuclear molecules; monomers; dimer; statistical associating fluids theory–dimer; equation of state of monomer–dimer mixtures.

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### 1. Introduction

Fluids containing heteronuclear chain molecules have been the subject of intense theoretical and technological interest in recent years. Main interest is focused on the development of equations of state of heteronuclear chain-like fluids such as copolymers. Copolymers are the chain molecules formed by simultaneous polymerization of two or more dissimilar monomers. These polymers are currently of great technological interest because their physical properties depend upon the chemical structure of the individual components. Thus, there is a great opportunity to form new materials with desirable properties for specific uses.

Several theoretical formalisms have been proposed to understand the microscopic behaviour of copolymers [1–3]. Chiew [4] proposed an equation of state to predict the thermodynamic properties of heteronuclear chain fluids and their mixtures. Recently, Gulati *et al* [5,6] have conducted a theoretical and molecular dynamics simulation study to understand the molecular thermodynamic behaviour of heteronuclear chain-like molecules. They have extended the generalized Flory (GF) and generalized Flory–dimer (GFD) equations of state to fluids containing hard heteronuclear chain-like molecules. The compressibility factors predicted by the

GFD theory for heteronuclear chain composed of block, alternating and random copolymer fluids are in very good agreement with their simulation results. Another approach developed by applying an extension to Wertheim's statistical associating fluid theory to homonuclear hard non-spherical fluids is known as statistical associating fluid-dimer theory. This was proposed by Ghonasgi and Chapman [7] and Chang and Sandler [8] at the same time. We have reformulated statistical associating fluid-dimer theory and applied it successfully to short-length chain molecules [9] as well as longer chain molecules [10]. Our results are in good agreement with simulation results obtained from GFD theory for homonuclear chain molecules. The present study proposes an application of the dimerized hard sphere theory to predict the equation of state of heteronuclear chain fluids. We assume that the chain is formed by alternating heteronuclear segments. Our approach is based on the idea that the equation of state for chain-like molecules can be constructed by judiciously combining the equations of state of the segments. Thus the dimer approach for homonuclear hard chains can be extended to the heteronuclear hard chains having alternating segments of different sizes by replacing the hard homo-monomers and hard homo-dimers by heteronuclear monomers and hard heteronuclear dimers respectively. The site-site correlation functions for heteronuclear monomers and heteronuclear dimers shall be obtained from their respective equations of state.

Yeom *et al* [11] developed a new equation of state for the freely jointed hard sphere chain fluid. They considered the equimolar mixtures of monomer and dimer fluids as an intermediate reference system by using multidensity Ornstein-Zernike (MOZ) integral equation theory. They have also performed MC simulation calculation for the contact values of the radial distribution function for the hard sphere dimer-monomer mixture and obtained a good agreement with their simulation results. We have extended this theory for heteronuclear chain fluids.

## 2. Theory

### 2.1 Statistical theory of associating dimerized chain fluids

We consider a fluid of pure hard copolymer which consists of two monomers A and B of different diameters. These two monomers A and B can form a heteronuclear disphere. The repetition of such dispheres can form heteronuclear alternating chain molecules. Thus a chain is formed by the polymerization of alternating heteronuclear segments.

Let us consider that the chain is formed by heteronuclear pairs of disphere. The equation of state of the heteronuclear dimer can be written by applying SAFT theory as

$$Z^{\text{HND}} = 2Z^{\text{HNM}} - \left( 1 + \eta \frac{\partial \ln g_{\text{HNM}}(\sigma)}{\partial \eta} \right), \quad (1)$$

where  $Z^{\text{HNM}}$  represents the normalized pressure ( $P/\rho k_{\text{B}}T$ ) of two monomers of different sizes of diameters  $\sigma_{\text{a}}$  and  $\sigma_{\text{b}}$ .  $g_{\text{HNM}}(\sigma)$  is the site-site correlation function at contact for heteronuclear monomers. Following dimer theory, we can write the pressure of alternating heteronuclear chain of  $m$ -segments as

$$Z^m = m Z^{\text{HNM}} - \frac{m}{2} \left( 1 + \eta \frac{\partial \ln g_{\text{HNM}}(\sigma)}{\partial \eta} \right) - \left( \frac{m}{2} - 1 \right) \left( 1 + \eta \frac{\partial \ln g_{\text{HND}}(\sigma)}{\partial \eta} \right). \quad (2)$$

Here  $g_{\text{HND}}(\sigma)$  is the site-site correlation function at contact for heteronuclear dimer. To determine site-site correlation function at contact for heteronuclear monomers ( $g_{\text{HNM}}(\sigma)$ ), we use the following relation:

$$Z^{\text{HNM}} = 1 + 4\eta g_{\text{HNM}}(\sigma), \quad (3)$$

where  $\eta = \rho V_m$  is the packing fraction of hard chains. The  $Z^{\text{HNM}}$  for heteronuclear monomers can be determined using the Mansoori-Carnahan-Starling-Leland (MCSL) equation [12]. We derive the simplified form of MCSL equation as

$$Z^{\text{HNM}} = 1 + \frac{\eta P}{(1 - \eta)^3}, \quad (4)$$

where

$$P = [(1 - \eta)^2 + 3(1 - \eta)K + D\eta(3 - \eta)].$$

Here

$$K = \frac{(1 + X)(1 + X^2)}{2(1 + X^3)}, \quad D = \frac{(1 + X^2)^3}{2(1 + X^3)^2} \quad \text{and} \quad X = \frac{\sigma_b}{\sigma_a}.$$

Hence,

$$g_{\text{HNM}}(\sigma) = \frac{P}{4(1 - \eta)^3}. \quad (5)$$

The site-site correlation function at contact for hard heteronuclear disphere  $g_{\text{HND}}(\sigma)$  can be determined through  $m$ -particle cavity correlation function (CCF) [13], as

$$Z^{\text{HND}} = 2Z^{\text{HNM}} - \left( 1 + \eta \frac{\partial \ln y_{ij}}{\partial \eta} \right), \quad (6)$$

where

$$\ln y_{ij} = \frac{aK\eta}{2(1 - \eta)} - \frac{bD}{2(1 - \eta)} + \frac{bD}{2(1 - \eta)^2} - cD \ln(1 - \eta) \quad (7)$$

with  $a = -0.61819$ ,  $b = 0.19421$ ,  $c = 2.75503$ . Thus we can solve that

$$g_{\text{HND}}(\sigma) = \frac{1}{4\eta} \left[ \frac{\eta}{(1 - \eta)} R + \frac{\eta}{(1 - \eta)^2} S + \frac{\eta}{(1 - \eta)^3} T \right]$$

$$R = \left\{ 2 - D(2 + c) + K \left( 6 - \frac{a}{2} \right) \right\},$$

$$S = \left\{ K\eta \left( 6 - \frac{a}{2} \right) - D \left( 2 - \frac{b}{2} \right) \right\},$$

$$T = \{ D(4 - b) \}. \quad (8)$$

Thus final expression for the equations of state of alternating  $m$ -heteronuclear hard chain in dimer theory can be written as

$$\begin{aligned}
 Z &= m \left[ 1 + \frac{\eta}{(1-n)^3} P \right] \\
 &\quad - \frac{m}{2} \left[ 1 + \eta \left\{ \frac{2\eta(1-D) + 3(D-K) - 2}{P} + \frac{3}{(1-\eta)} \right\} \right] \\
 &\quad - \left( \frac{m}{2} - 1 \right) \left[ 1 + \frac{\eta Q}{[(1-\eta)^2 R + (1-\eta)S + T]} + \frac{3\eta}{(1-\eta)} \right], \quad (9) \\
 Q &= \left[ (2\eta - 2) \{2 - D(2+c)\} - K \left(6 - \frac{a}{2}\right) + D \left(2 - \frac{b}{2}\right) \right].
 \end{aligned}$$

The quantity  $g_{\text{HND}}(\sigma)$  can also be determined by employing scaled particle theory. We choose the equation of state for non-spherical hard body system proposed by Boublik [14]. The general form of EOS is given by

$$\begin{aligned}
 Z^{\text{HND}} &= \frac{1}{(1-\eta)} + \frac{3\alpha\eta}{(1-\eta)^2} \\
 &\quad + \frac{\eta^2 [(49\alpha - 31) - \eta(11\alpha - 7) - \eta^2(25\alpha - 21)]}{6(1-\eta)^3}, \quad (10)
 \end{aligned}$$

where  $\alpha$  is the non-sphericity parameter. The parameter  $\alpha$  is defined in terms of the  $1/4\pi$  multiple of the mean curvature integral  $R_m$ , the surface area  $S_m$  and the volume  $V_m$  of the molecule as

$$\alpha = \frac{R_m S_m}{3V_m} = \frac{\{1 + X^2\} \{1 + X^2 + X\}}{\{1 + X\} \{1 + X^3\}}. \quad (11)$$

The numerical determination of  $\partial \ln g_{\text{HND}}(\sigma) / \partial \eta$  can be derived as

$$\begin{aligned}
 &\frac{\partial \ln g_{\text{HND}}(\sigma)}{\partial \eta} \\
 &= \frac{[(31\alpha - 43) + 2\eta(13 - 11\alpha) + 3\eta^2(21 - 25\alpha)]}{[(18\alpha + 6) + (31\alpha - 43)\eta + (13 - 11\alpha)\eta^2 + (21 - 25\alpha)\eta^3]} \\
 &\quad + \frac{3}{(1-\eta)}. \quad (12)
 \end{aligned}$$

## 2.2 Statistical fluid theory of associating monomer-dimer mixture

We consider a fluid of pure hard copolymer which consists of two monomers A and B of different diameters. These two monomers A and B polymerize to form heteronuclear disphere, a trimer is formed from dimer and monomer of type A and a  $m$ -mer from a  $(m-1)$  mer and a monomer. Thus following MOZ integral equation

theory, we can write the Helmholtz energy change due to the formation of  $m$ -mer chain [11] as

$$\begin{aligned} \frac{A^{\text{chain}}}{NKT} &= -\ln g^{\text{HNM}}(1,1) - (m-2) \ln g^{\text{MDM}}(2,1) \\ &= -\ln g^{\text{HNM}}(\sigma) - (m-2) \ln g^{\text{MDM}}(\sigma), \end{aligned} \quad (13)$$

where  $g^{\text{HNM}}(1,1)$  is the expression for the contact value of the correlation function of two heteronuclear monomers and  $g^{\text{MDM}}(2,1)$  is the correlation function of heteronuclear dimer and a monomer mixture (MDM) evaluated at the bond length.

The expression for the contact values of the correlation function of monomer-dimer mixture can be written by following the MOZ theory [15].

$$g^{\text{MDM}}(2,1) = g^{\text{HNM}}(\sigma) - \frac{1}{4(1-\eta)}. \quad (14)$$

Here  $g^{\text{HNM}}(\sigma) = g_{\text{HNM}}(\sigma)$ , i.e., eq. (5).

The pressure  $m$ -mer chain can be written as

$$Z = mZ^{\text{HNM}} + Z^{\text{chain}}, \quad (15)$$

where  $Z^{\text{HNM}}$  for the heteronuclear monomers can be calculated by following Mansoori-Carnahan-Starling-Leland equation of state [12] which is described by eq. (4) for heteronuclear monomers and the equation of state for  $Z^{\text{chain}}$  is given by

$$Z^{\text{chain}} = - \left\{ 1 + \eta \frac{\partial \ln g^{\text{HNM}}(\sigma)}{\partial \eta} \right\} - (m-2) \left\{ 1 + \eta \frac{\partial \ln g^{\text{MDM}}(\sigma)}{\partial \eta} \right\}. \quad (16)$$

The value of  $g^{\text{HNM}}(\sigma)$  is already described by eq. (5) and  $g^{\text{MDM}}(\sigma)$  can be obtained by substituting eq. (5) in eq. (14) as

$$g^{\text{MDM}}(\sigma) = \frac{[3(1-\eta)K + D\eta(3-\eta)]}{4(1-\eta)^3}. \quad (17)$$

Thus the equation of state for alternating heteronuclear chain molecules can be written as

$$\begin{aligned} Z &= m \left[ 1 + \frac{\eta}{(1-\eta)^3} P \right] \\ &\quad - \left[ 1 + \eta \left\{ \frac{2\eta(1-D) + 3(D-K) - 2}{P} + \frac{3}{(1-\eta)} \right\} \right] \\ &\quad - (m-2) \left[ 1 + \eta \left\{ \frac{[3(D-K) - 2\eta D]}{[3(1-\eta)K + D\eta(3-\eta)]} + \frac{3}{(1-\eta)} \right\} \right]. \end{aligned} \quad (18)$$

The Helmholtz energy of a chain fluid is written as

$$\frac{A}{NKT} = \frac{A^{\text{ideal}}}{NKT} + \frac{A^{\text{mono}}}{NKT} + \frac{A^{\text{chain}}}{NKT}, \quad (19)$$

where  $N$  is the total number of chains,  $T$  is the temperature,  $K$  is the Boltzman's constant.  $A^{\text{ideal}}$ ,  $A^{\text{mono}}$  and  $A^{\text{chain}}$  are the Helmholtz energies of ideal, monomer [12] and chain contributions [11] respectively. Hence, we find

$$\begin{aligned} \frac{A}{NKT} = & \ln \left( \frac{6\eta}{\pi m} \right) - 1 \\ & + m \left\{ \frac{3K\eta - D}{(1-\eta)} + \frac{D}{(1-\eta)^2} + (D-1) \ln(1-\eta) \right\} \\ & - \ln \left[ \frac{P}{4(1-\eta)^3} \right] - (m-2) \left[ \frac{[3(1-\eta)K + D\eta(3-\eta)]}{4(1-\eta)^3} \right]. \end{aligned} \quad (20)$$

The chemical potential can be determined with the help of Helmholtz energy by the relation

$$\frac{\beta\mu}{N} = \frac{\partial}{\partial \eta} \eta \left( \frac{\beta A}{N} \right), \quad \text{where } \beta = \frac{1}{KT}. \quad (21)$$

Therefore the chemical potential for the present work can be written as

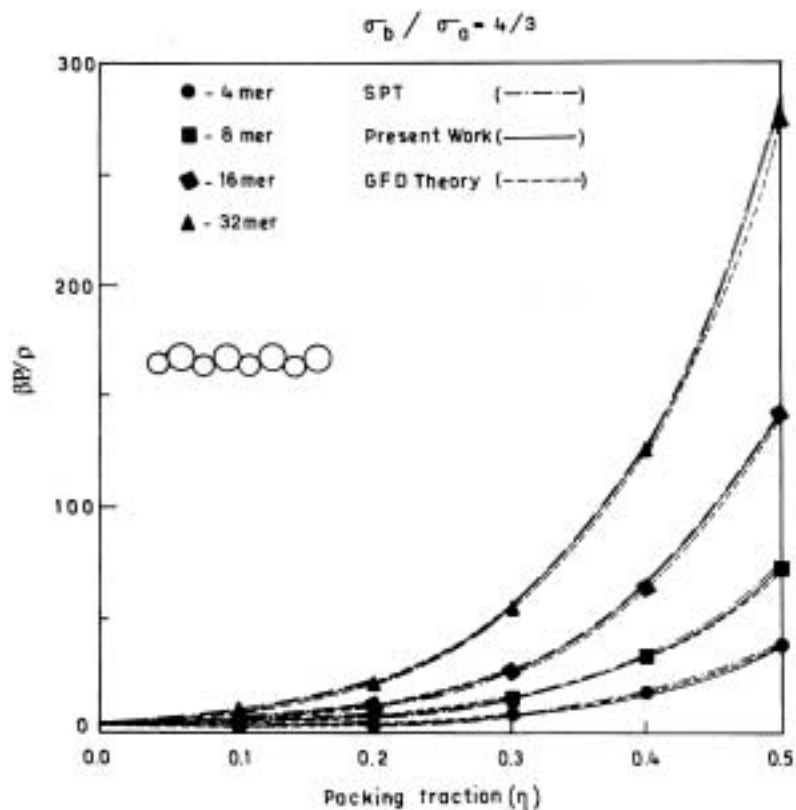
$$\begin{aligned} \frac{\beta\mu}{N} = & \ln \left( \frac{6\eta}{\pi m} \right) + \left\{ \frac{2\eta(3K + D) + 3K\eta^2(\eta - 3)}{(1-\eta)^3} \right\} \\ & + (D-1) \left\{ \ln(1-\eta) - \frac{\eta}{(1-\eta)} \right\} \\ & - \left[ \eta \left\{ \frac{2\eta(1-D) + 3(D-K) - 2}{P} + \frac{3}{(1-\eta)} \right\} \right] \\ & + \ln \left\{ \frac{P}{4(1-\eta)^3} \right\} - (m-2) \\ & \times \left[ \eta \left\{ \frac{[3(D-K) - 2\eta D]}{[3(1-\eta)K + D\eta(3-\eta)]} + \frac{3}{(1-\eta)} \right\} \right] \\ & + \ln \left\{ \frac{3(1-\eta)K + D\eta(3-\eta)}{4(1-\eta)^3} \right\}. \end{aligned} \quad (22)$$

### 3. Results and discussion

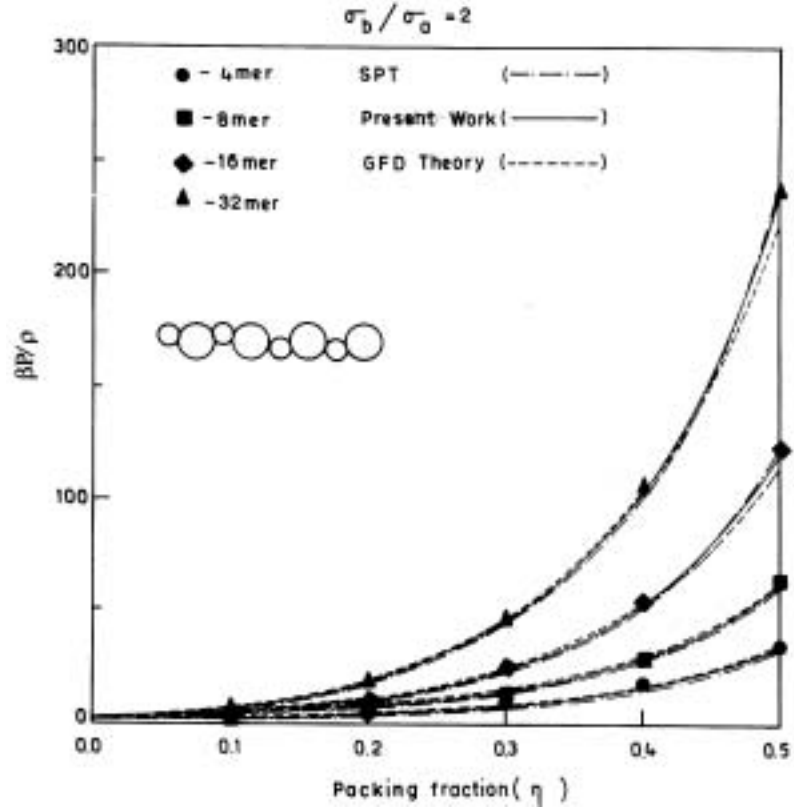
#### 3.1 Dimerized chain fluid theory

We consider a fluid consisting of two monomer hard spheres of different diameters  $\sigma_a$  and  $\sigma_b$  polymerize to form heteronuclear disphere. These heteronuclear hard molecules polymerize to form a tangent chain which consists of alternating segments

of different sizes. Thus a chain of alternating segments AB, AB, AB can form  $m$ -mers chain lengths. In this work, we emphasize that a heteronuclear dimer can form a chain of alternating copolymers and equation of state of alternating copolymers having  $m$ -segments can be determined by using the simple dimer theory. By employing eq. (9), we have evaluated the equations of state of 4-, 8-, 16- and 32-mers for heteronuclear spheres of size ratio  $\sigma_b/\sigma_a = 4/3$  and  $\sigma_b/\sigma_a = 2$ . In order to test the present work based on dimerized chain fluid theory, we compare our results with those obtained by GFD theory [5] and also with molecular dynamics data [5]. Figures 1 and 2 show our results for 4-, 8-, 16- and 32-mers heteronuclear alternating segment chains with a size ratio of  $\sigma_b/\sigma_a = 4/3$  and  $\sigma_b/\sigma_a = 2$  respectively as a function of packing fraction. The filled symbols represent MD simulation results [5]. A comparison between the present work and MD values reveals that dimer theory can describe the pressure of heteronuclear alternating chain at various densities satisfactorily. However, at higher packing fractions a discrepancy arise between theoretical and MD simulation results for higher mers such as 32-mers as shown in



**Figure 1.** Equation of state ( $Z = \beta P/\rho$ ) of the alternating copolymer for 4-, 8-, 16- and 32-mers at  $\sigma_b/\sigma_a = 4/3$ . Filled symbols represent MD simulation results and curves represent the predictions of statistical associating fluid theory-dimer, scaled particle and GFD theories.



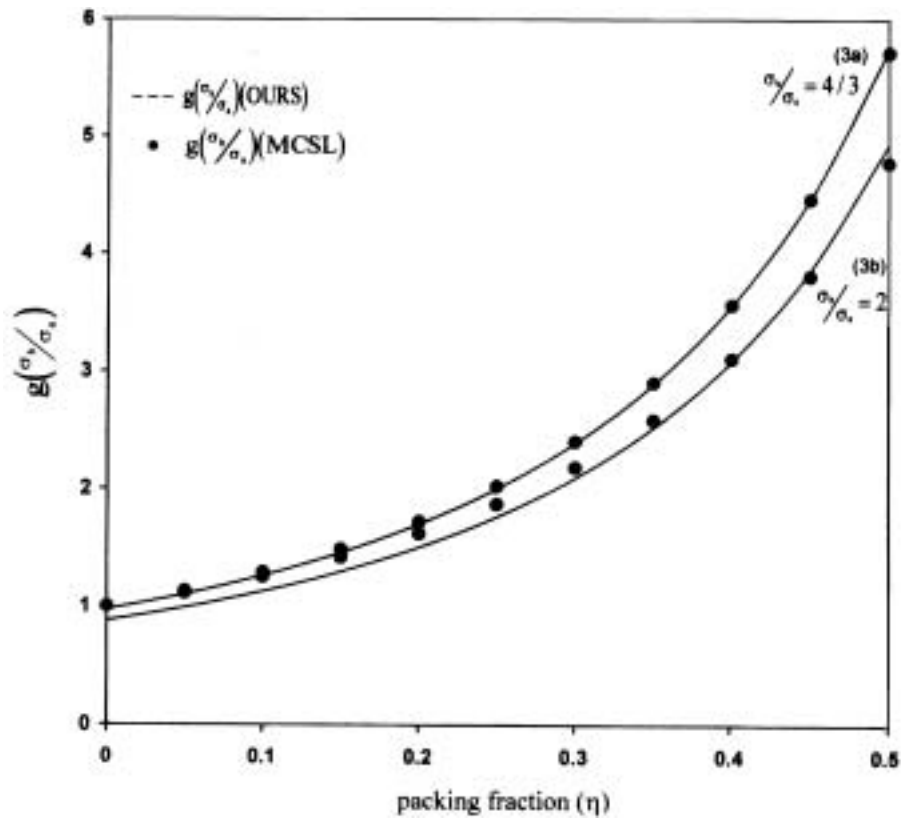
**Figure 2.** Equation of state ( $Z = \beta P/\rho$ ) of the alternating copolymer for 4-, 8-, 16- and 32-mers at  $\sigma_b/\sigma_a = 2$ . Filled symbols represent MD simulation results and curves represent the predictions of statistical associating fluid theory-dimer, scaled particle and GFD theories.

figure 1. Present work predicts somewhat higher values than the values predicted by the GFD theory at high densities for higher mers, which makes the results better for  $\sigma_b/\sigma_a = 2$ . It is due to the fact that GFD theory slightly underestimates the pressure at high densities.

To show that the pair correlation function at contact of heteronuclear monomer fluid is quite adequate, we compare our results with those obtained by MCSL formulae. Recently, Grundke and Henderson [16] obtained the correlation function at contact for hard sphere mixture employing MCSL equation of state. Equation (6) of [16] can be solved for two hard spheres having diameter  $\sigma_a$  and  $\sigma_b$  and can be written in terms of  $\sigma_b/\sigma_a$  as

$$g\left(\frac{\sigma_b}{\sigma_a}\right) = \frac{1}{(1-\eta)} + \frac{3\eta(1+\Delta^2)\Delta}{(1+\Delta^3)(1-\eta)^2(1+\Delta)} + \frac{2\eta^2\Delta^2(1+\Delta^2)^2}{(1+\Delta^3)^2(1+\Delta)^2(1-\eta)^3} \tag{23}$$



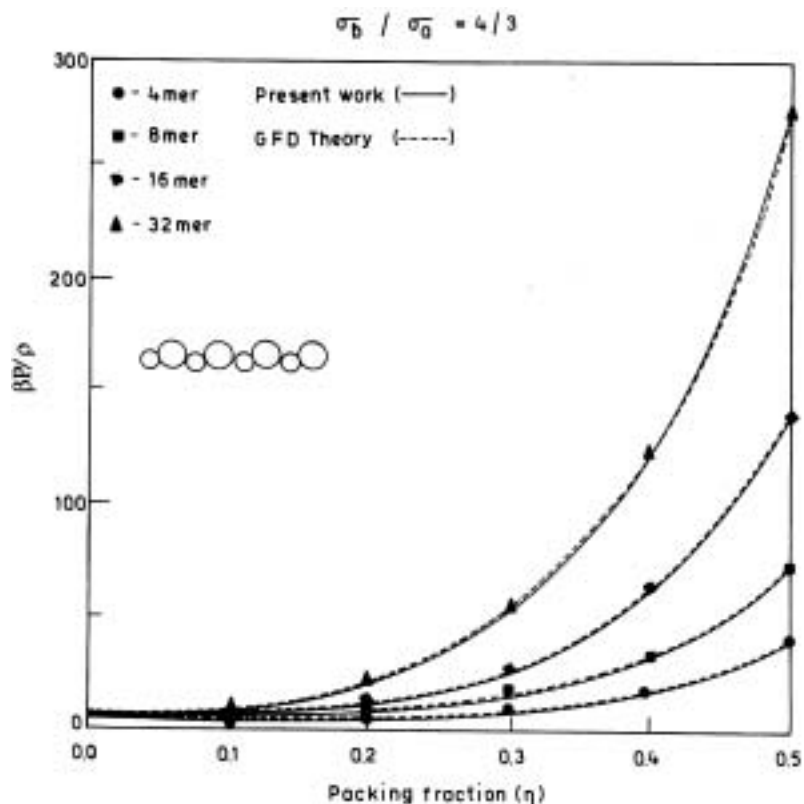


**Figure 3.** Comparison between present work and MCSL values of the contact values of the radial distribution function for the heteronuclear hard sphere monomers at  $\sigma_b/\sigma_a = 4/3$  and  $\sigma_b/\sigma_a = 2$ .

We have computed the values of  $g(\sigma_b/\sigma_a)$  using eq. (23) for packing fraction 0.05 to 0.5 and for  $\sigma_b/\sigma_a = 4/3$  and 2. We find an excellent agreement between the values calculated from (23) and from eq. (5) for  $\sigma_b/\sigma_a = 4/3$  as shown in figure 3a. However, a small deviation is observed between  $g^{\text{MCSL}}(\sigma_b/\sigma_a)$  (eq. (23)) and  $g^{\text{OUR}}(\sigma_b/\sigma_a)$  (eq. (5)) for  $\sigma_b/\sigma_a = 2$  as shown in figure 3b. This shows the validity of eq. (3) for finding the site-site correlation function at contact for heteronuclear monomers for small and medium size ratio of hard sphere diameters.

### 3.2 Scaled particle theory

The equations of state of 4-, 8-, 16- and 32-mers are evaluated by employing scaled particle theory (eq. (10)) for  $\sigma_b/\sigma_a = 4/3$  and 2. We find that scaled particle theory predicts higher values of equation of state as shown in figures 1 and 2 and in poor agreement with MD simulation values in comparison to dimer theory and GFD theory.

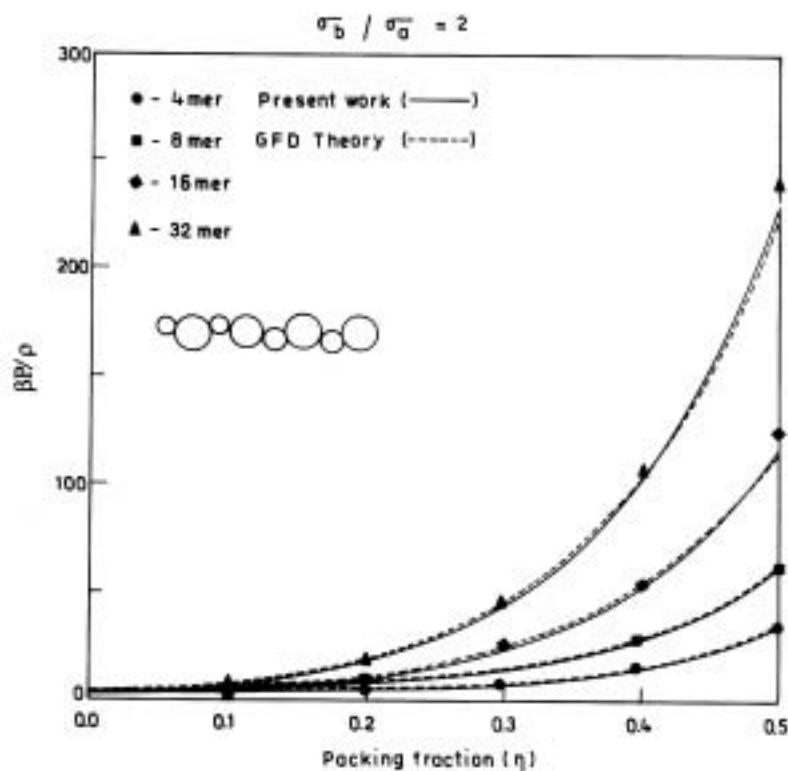


**Figure 4.** Equation of state ( $Z = \beta P/\rho$ ) of the alternating heteronuclear chain for 4-, 8-, 16- and 32-mers at  $\sigma_b/\sigma_a = 4/3$ . Filled symbols represent MD simulation results and curves represent the predictions of the monomer–dimer mixture and GFD theories.

### 3.3 Equation of state of monomer–dimer mixture

We consider an intermediate reference system [11] of the dimer and monomer that polymerized in a different way than in dimer theory. In sequential polymerization, a dimer is formed from two heteronuclear monomers, a trimer is formed from a heteronuclear dimer and a monomer such that the sequence of alternating segments of different diameters does not alter and so on we form a chain. Let  $g(K, 1)$  is the contact value of radial distribution function between an end segment of a  $K$ -mer and a monomer. For simplicity, we assume that  $g(K, 1)$  is nearly insensitive to  $K$  and is nearly the same as  $g(2, 1)$  for  $K \geq 2$ . We also consider that monomers are formed of components having diameters  $\sigma_a$  and  $\sigma_b$  forming alternating heteronuclear chain and thus equation of state proposed by MCSL is used instead of Carnahan and Starling for hard sphere reference system.

We compare our results obtained from eq. (18), for the hard sphere chain fluids composed of 4-, 8- and 16-mers with the predictions of Gulati *et al's* [5] theoretical



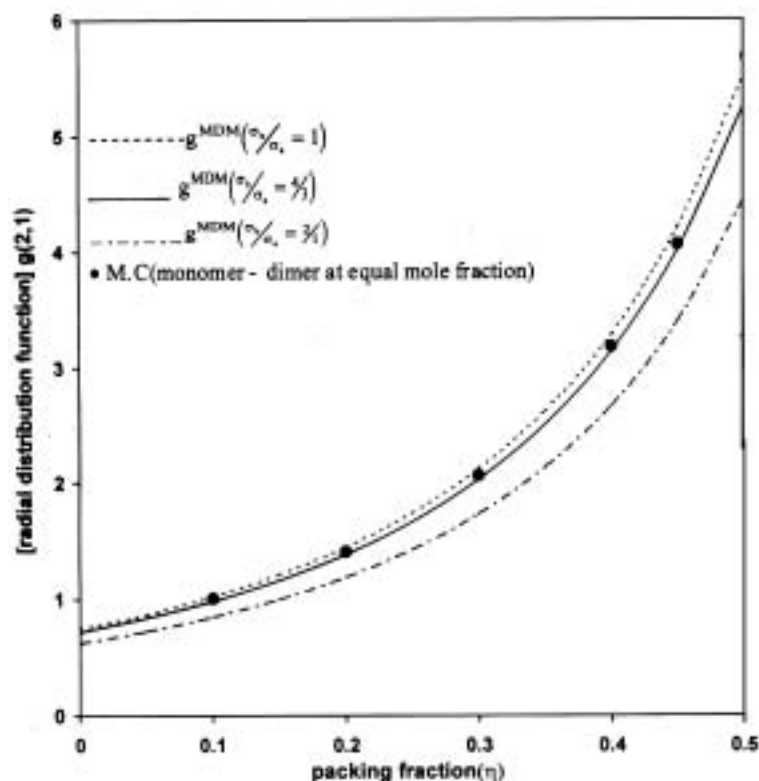
**Figure 5.** Equation of state ( $Z = \beta P/\rho$ ) of the alternating heteronuclear chain for 4-, 8-, 16- and 32-mers at  $\sigma_b/\sigma_a = 2$ . Filled symbols represent MD simulation results and curves represent the predictions of the monomer-dimer mixture and GFD theories.

and simulation results for  $\sigma_b/\sigma_a = 4/3$  and  $\sigma_b/\sigma_a = 2$ . We find a good agreement with simulation results as shown in figures 4 and 5, except the results of 16-mers and 32-mers for  $\sigma_b/\sigma_a = 2$ . This may show the limitation of the theory for higher mers with large size ratio of hard sphere diameters.

In the present model, the equation of state is dependent on the contact values of the correlation function of monomer and of monomer-dimer mixture. In figure 6, we have plotted the contact value of the radial distribution functions  $g^{\text{MDM}}(\sigma)$  ( $= g(2, 1)$ ) of monomer-dimer mixture for  $\sigma_b/\sigma_a = 1, 4/3$  and 2. We find that the value of  $g^{\text{MDM}}(\sigma)$  decreases with the increase in ratio of the segment diameters. For  $\sigma_b/\sigma_a = 1$ , we find that our values of  $g^{\text{MDM}}(\sigma)$  show a good agreement with the simulation values tabulated in table 1 of [11].

#### 4. Conclusion

Our aim of the present work is to demonstrate the usefulness of the statistical associating fluid-dimer theory to predict the compressibility factor of alternating



**Figure 6.** The contact values of the radial distribution function  $g(2,1)$  for the alternating heteronuclear monomer-dimer mixture hard sphere at  $\sigma_b/\sigma_a = 1, 4/3$  and 2.

heteronuclear chain molecules. The work can be further extended to block and random copolymers. In another work, we have also demonstrated the usefulness of the dimer theory in predicting residual chemical potential. More correct estimation of the pair correlation functions may lead to better estimation of the physical properties of chain fluids than GFD theory.

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