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Publisher *Taylor & Francis*

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Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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To cite this Article Singh, Dinesh Kumar and Khanna, K. N.(2004) 'Statistical associating Fluid Dimer Theory', *Physics and Chemistry of Liquids*, 42: 3, 237 – 243

To link to this Article: DOI: 10.1080/00319100310001632370

URL: <http://dx.doi.org/10.1080/00319100310001632370>

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STATISTICAL ASSOCIATING FLUID DIMER THEORY

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(Received 2 April 2003)

Three modified versions of statistical associating fluid theory known as SAFT-D1, SAFT-D2 and SAFT-T for hard sphere chain molecules are used to test the approximation made in the derivation of the statistical associating fluid dimer theory (SAFT-D). The SAFT-D1 model accounts for the chain length independent site–site correlation function at contact, while SAFT-D2 and SAFT-T models account for chain length dependent site–site correlation function at contact. The residual chemical potentials are calculated for hard chain fluids containing chains of length $m = 3, 4, 6, 8, 12, 16$ and 32 mers and compared with the results obtained by configurational bias Monte Carlo (MC) method at various densities. We find that the approximation used in SAFT-D1 theory leads to an over prediction of residual chemical potential and its magnitude increases with increasing chain length.

Keywords: SAFT-D; Chain length; Monte Carlo

INTRODUCTION

In recent years, several equations of state have been developed for hard-sphere chain fluids, based on statistical mechanical theory [1,2] as it can serve as the backbone to build more realistic models. The extension of Wertheim theory [1] resulted in an equation of state for associating chain molecules called the statistical associating fluid theory (SAFT) [3,4]. SAFT predicts poor results for EOS and second virial coefficient for longer chain length. Ghonasgi and Chapman [5] and Chang and Sandler [6] have improved SAFT by introducing hard chain dimer reference system, while Johnson [7] derived the Lennard–Jones (LJ) dimer reference system.

On a different line of approach, Dickman and Hall [8] and Honnell and Hall [9] derived the generalized Flory (GF), the generalized Flory–Huggins (GFH) and generalized Flory dimer (GFD) equations of state for the hard sphere chains fluids. Thus two important theories are the GFD [9] and statistical associating Fluid theory-dimer (SAFT-D) [5]. GFD theory is developed on the assumption that the probability of inserting a test chain into chain fluids can be related to the probabilities of inserting a monomer into a monomer fluid and dimer into a dimer fluid. The GFD theory underestimates the probability of inserting a monomer into a chain fluid by $\leq 40\%$ at liquid

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density. The errors associated with the probability of inserting the second bead next to the first bead in dimer fluid are much lower $\leq 10\%$. In spite of these errors, GFD theory does well in predicting equation of state of chain fluids due to cancellation of errors. Recently, Kumar *et al.* [10] have tested the GFD theory by predicting the chemical potential over a wide range of densities. The figure of merit that they have used in the test is the residual chemical potential μ^r minus the zero density chemical potential $\{\mu^r(\rho)=0\}$, and this is related to the insertion probability $P_n(\eta)$ through the expression $\mu^r - \mu^r(\eta=0) = -kT \ln P_n(\eta)$. SAFT-D theory [5] also suffers from inconsistency with Monte Carlo (MC) values at packing fractions higher than 0.35 and with increasing chain length. The equation of state in SAFT-D theory requires only the contact values of the hard sphere correlation function and hard disphere site–site correlation function $g(\sigma)$. Ghonasgi and Chapman [5] have employed the expression of $g(\sigma)$ of the dimer with an assumption that the correlation function at contact of the dimer, tetramer, octamer and so on will remain the same. The theory can be applied readily to molecules having longer chain lengths. We have re-examined the equation of state of the SAFT-D theory [11]. In this work we have employed the contact value of the correlation function $g(\sigma)$ proposed by Chiew [12] who has derived analytical expression for the average correlation function at contact as a function of chain length m and hard sphere volume function η . We have employed the expression of $g(\sigma)$ for m components separately without making any assumption. We have found that our equation of state predicts better results than those obtained by Ghonasgi and Chapman [5]. However, the equation of state is not very sensitive to the errors associated with the approximations assumed in theory. Thus, it is important to evaluate the accuracy of the approximations. In the present work, we have examined the accuracy of our proposed equation of state by finding the residual chemical potential and compared with SAFT-D (now referred as SAFT-D1) proposed by Ghonasgi and Chapman. Thus the aim of the present work is to show that the residual chemical potential ($\mu^r - \mu^r(\eta=0)$) associated with modified SAFT-D (now referred to as SAFT-D2) equation of state predicts better values than the SAFT-D1 model and in good agreement with the results obtained through configurational bias Monte Carlo method (CBMC) by Kumar *et al.* [10]. This results from the importance of m site–site correlation function at contact considered in the our work [11] in comparison to dimer correlation function at contact considered to be the same for all chain lengths by Ghonasgi and Chapman [5].

Recently, we have also proposed a new equation of state of chain molecules using SAFT [13]. The formalism derived is based on the assumption that chain is formed by the pair of trimers. In this model, we have further applied the site–site correlation function at contact as a function of a chain length instead of assuming an approximation that the correlation function is independent of chain length. Thus, it is worthwhile to include this model for comparison with SAFT-D1 model.

THEORY

From the knowledge of the equation of state (Z) of hard sphere chain fluid, one can obtain the residual Helmholtz free energy as

$$\frac{\beta A^{\text{res}}}{N} = \int_0^\eta (Z - 1) \frac{\delta \eta}{\eta} \quad (1)$$

From the residual Helmholtz free energy, one can obtain the residual chemical potential μ^{res} , as follows

$$\beta\mu^{\text{res}} = \frac{\delta}{\delta\eta} \left[\eta \frac{\beta A^{\text{res}}}{N} \right] \quad (2)$$

In the present work, we have employed three models based on the SAFT theory known as SAFT-D1 model proposed by Ghonasgi and Chapman and two models SAFT-D2 and SAFT-T, proposed by us [11,13].

(i) SAFT-D1 model The equation of state of SAFT-D1 model [5] is written as

$$Z = mZ^{\text{HS}} - \frac{m}{2} \left[1 + \frac{\eta(5-2\eta)}{(1-\eta)(2-\eta)} \right] - \left(\frac{m}{2} - 1 \right) \left[1 + \frac{2\eta(2+\eta)}{(1-\eta)(1+2\eta)} \right] \quad (3)$$

The expression for residual Helmholtz free energy and chemical potential can be derived as

$$\frac{\beta A^{\text{res}}}{N} = \frac{m(4\eta - 3\eta^2)}{(1-\eta)^2} + \frac{m}{2} \ln \frac{2(1-\eta)^3}{(2-\eta)} - (m-2) \ln \frac{(1+2\eta)^{1/2}}{(1-\eta)} \quad (4)$$

$$\begin{aligned} \beta\mu^{\text{res}} = m & \left(\frac{8\eta - 9\eta^2 + 3\eta^3}{(1-\eta)^3} \right) - \frac{m}{2} \left[\frac{(5\eta - 2\eta^2)}{(1-\eta)(2-\eta)} + \ln \frac{(2-\eta)}{2(1-\eta)^3} \right] \\ & - (m-2) \left[\frac{\eta(2-\eta)}{(1-\eta)(2-\eta)} + \ln \frac{(1+2\eta)^{1/2}}{(1-\eta)} \right] \end{aligned} \quad (5)$$

(ii) SAFT-D2 model SAFT-D1 theory is reformulated to yield an improved equation of state for the hard sphere chain fluid and is given by [11].

$$\begin{aligned} Z = mZ^{\text{HS}} - (m-1) - \frac{\eta}{(1-\eta)} & \left\{ \frac{m(5-2\eta)}{2(2-\eta)} + \frac{m2(2+\eta)}{4(1+2\eta)} + \frac{m(5+3\eta)}{8(1+3\eta)} \right. \\ & \left. + \frac{m(29+19\eta)}{16(5+19\eta)} + \frac{m(57+39\eta)}{32(9+39\eta)} \right\} \end{aligned} \quad (6)$$

The Helmholtz free energy and residual chemical potential of Eq. (6) can now be derived as

$$\begin{aligned} \frac{\beta A^{\text{res}}}{N} = \frac{m(4\eta - 3\eta^2)}{(1-\eta)^2} - \frac{m}{2} & \left[\ln \frac{(2-\eta)}{2(1-\eta)^3} \right] - \frac{m}{4} 2 \left[\frac{(1+2\eta)^{1/2}}{(1-\eta)} \right] \\ & - \frac{m}{8} \ln \left[\frac{(1+3\eta)}{(1-\eta)^2} \right] - \frac{m}{16} \ln \left[\frac{(5+19\eta)}{5(1-\eta)^2} \right] \end{aligned} \quad (7)$$

$$\begin{aligned} \beta\mu^{\text{res}} = & m \left(\frac{8\eta - 9\eta^2 + 3\eta^3}{(1-\eta)^3} \right) - \frac{m}{2} \left(\frac{(5\eta - 2\eta^2)}{(1-\eta)(2-\eta)} + \ln \frac{(2-\eta)}{2(1-\eta)^3} \right) \\ & - \frac{m}{4} 2 \left(\frac{\eta(2-\eta)}{(1-\eta)(1+2\eta)} + \ln \frac{(1+2\eta)^{1/2}}{(1-\eta)} \right) - \frac{m}{8} \left(\frac{(5\eta + 3\eta^2)}{(1-\eta)(1+3\eta)} + \ln \frac{(1+3\eta)}{(1-\eta)^2} \right) \\ & - \frac{m}{16} \left(\frac{(29\eta + 19\eta^2)}{(1-\eta)(5+19\eta)} + \frac{(5+19\eta)}{5(1-\eta)^2} \right) \end{aligned} \quad (8)$$

(iii) SAFT-T model (Trimer model) The equation of state for m -mers in, the trimer model can be written as [13].

$$\begin{aligned} Z^m = mZ^{\text{HS}} - (m-1) - \frac{\eta}{(1-\eta)} \left\{ \frac{2}{3} m \frac{(5-2\eta)}{(2-\eta)} + \frac{m(23+13\eta)}{6(5+13\eta)} + \frac{m(11+7\eta)}{12(2+7\eta)} \right. \\ \left. + \frac{m(43+29\eta)}{24(7+29\eta)} + \dots \right\} \end{aligned} \quad (9)$$

The Helmholtz free energy and residual chemical potential for trimer model can be derived as

$$\begin{aligned} \frac{\beta A^{\text{res}}}{N} = & m \frac{(4\eta - 3\eta^2)}{(1-\eta)^2} - \frac{2}{3} m \left\{ \ln \frac{(2-\eta)}{2(1-\eta)^3} \right\} - \frac{m}{6} \left\{ \ln \frac{(5+13\eta)}{5(1-\eta)^2} \right\} - \frac{m}{12} \left\{ \ln \frac{(2+7\eta)}{2(1-\eta)^2} \right\} \\ & - \frac{m}{24} \left\{ \ln \frac{(7+29\eta)}{7(1-\eta)^2} \right\} \end{aligned} \quad (10)$$

and

$$\begin{aligned} \beta\mu^{\text{res}} = & m \left\{ \frac{8\eta - 9\eta^2 + 3\eta^3}{(1-\eta)^3} \right\} - \frac{2}{3} m \left\{ \frac{(5\eta - 2\eta^2)}{(1-\eta)(2-\eta)} + \ln \frac{(2-\eta)}{2(1-\eta)^3} \right\} \\ & - \frac{m}{6} \left\{ \frac{(23\eta + 13\eta^2)}{(1-\eta)(5+13\eta)} + \ln \frac{(5+13\eta)}{5(1-\eta)^2} \right\} - \frac{m}{12} \left\{ \frac{(11\eta + 7\eta^2)}{(1-\eta)(2+7\eta)} + \ln \frac{(2+7\eta)}{2(1-\eta)^2} \right\} \\ & - \frac{m}{24} \left\{ \frac{(33\eta + 29\eta^2)}{(1-\eta)(7+29\eta)} + \ln \frac{(7+29\eta)}{7(1-\eta)^2} \right\} \end{aligned} \quad (11)$$

where Z^{HS} is the equation of state for hard spheres [14] and is given by

$$Z^{\text{HS}} = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3}$$

and $\beta\mu^{\text{res}}(\eta=0) = 0$ from Eqs. (5), (8) and (11).

RESULTS AND DISCUSSION

The accuracy of the SAFT-D theory is dependent on the accurate representation of the site–site correlation function for disphere and the groups of segments. The figure of merit, that we have used in the present work, is the numerical determination of residual chemical potential ($\mu^r - \mu^r(\eta=0)$) for hard chain fluids containing chains of length $m=2, 4, 6, 8, 12, 16$ and 24 . The value of $\mu^r(\eta=0)$ is zero in all three Eqs. (5), (8) and (11). We now consider how the Eqs. (6) and (9) are different from Eq. (3). Firstly, we examine the accuracy of dimer. Figure 1 shows the results of the residual chemical potential of dimer of the SAFT-D1 or SAFT-D2 (both are same) with that of Tildesley–Streett expression [15] that is given by

$$\frac{\mu^{\text{res}}(\eta, 2)}{KT} = \left[\frac{13.66895\eta - 13.417225\eta^2 + 3.554065\eta^3}{(1 - \eta)^3} \right] + 2.75503 \ln(1 - \eta)$$

We find excellent accord between two results which means that the discrepancy arises for higher mers. Figure 2 shows the residual chemical potential for 4, 8 and 16 mers employing the SAFT-D2 model. Comparison with the SAFT-D1 model shows that the discrepancy between SAFT-D1 and SAFT-D2 models increases with the increase of chain length. The result for the residual chemical potential obtained for SAFT-D2 model shows good agreement with results obtained from configurational bias MC method. The numerical values of CBMC method are determined using Eq. (32) and Table I of the Ref. [10]. Similarly, Fig. 3 shows the residual chemical potential for 6, 12 and 24 mers employing SAFT-T model and MC values. We find the discrepancy between SAFT-D1 model and SAFT-T model increases with the increase of chain length. MC values for 6, 12 and 24 mers are obtained by considering mean values of the respective mers given in the Table I of the Ref. [10]. For example for 6 mers, we have considered the mean values of 4 and 8 mers.

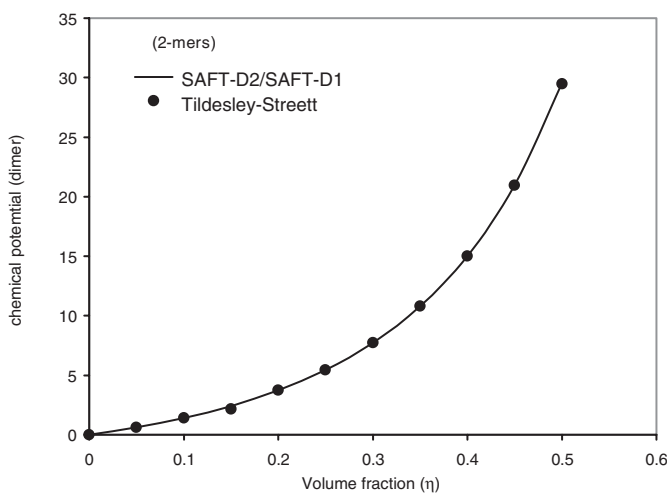


FIGURE 1 Comparison between the Tildesley and Streett values (circles) and SAFT-D2 predictions (solid line) of the chemical potential (μ^r/KT) for dimer.

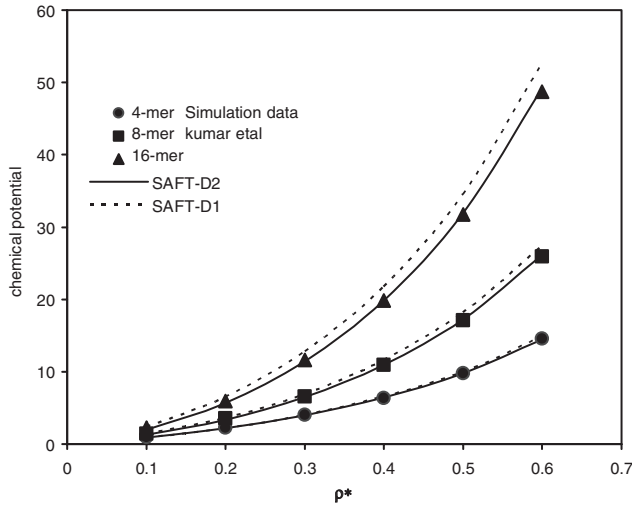


FIGURE 2 Comparison of the chemical potential (μ^r/KT) between SAFT-D1 and SAFT-D2 predictions with simulation values [10] for 4, 8 and 16 mers [$\rho^* = 6\eta/\pi$].

TABLE I Comparison of the chemical potential from SAFT-D1, SAFT-D2 and SAFT-T models with Monte Carlo data [16]. (μ/KT) = (μ^r/KT) + ideal term

m	η_f	Model	μ/KT
4	0.5289	SAFT-D1	67.41
		SAFT-D2	66.25
		MC	65.82
8	0.5393	SAFT-D1	142.82
		SAFT-D2	138.9
		MC	133.9
3	0.5288	SAFT-D1	51.42
		Trimer	50.85
		MC	49.01
6	0.5393	SAFT-D1	107.92
		Trimer	105.26
		MC	101.75

We now discuss the comparison of the residual chemical potential at higher densities. Table I shows the comparison of residual chemical potential of SAFT-D1, SAFT-D2 and SAFT-T models with MC data at high densities [16]. We find that the SAFT-D2 and SAFT-T models predict better results than those obtained from the SAFT-D1 model.

CONCLUSION

The contact value of the correlation function at contact plays an important role in describing thermodynamic properties of the hard sphere chain molecules and its accuracy is more important with increasing chain length. Another interesting issue concerned with the accuracy of the correlation function at contact is the possibility of

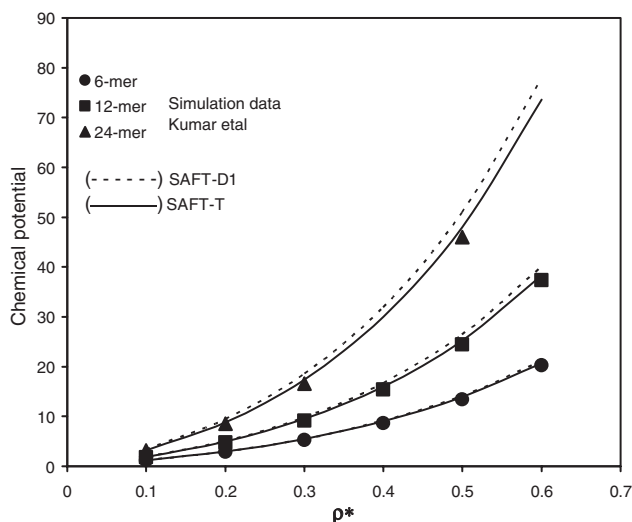


FIGURE 3 Comparison of the chemical potential (μ^r/KT) between SAFT-D1 and SAFT-T predictions with simulation values [10] for 6, 12 and 24 mers [$\rho^* = 6\eta/\pi$].

quantitative change in fluid–solid phase equilibrium. Finally, the present work reflects that the properties of a chain fluid are built up segment-by-segment or in-group of segments in the SAFT-D theory similar to GFD theory.

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