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Development of the Semi-empirical Equation of State for Square-well Chain Fluid Based on the Statistical Associating Fluid Theory (SAFT)

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Abstract–A semi-empirical equation of state for the freely jointed square-well chain fluid is developed. This equation of state is based on Wertheim's thermodynamic perturbation theory (TPT) and the statistical associating fluid theory (SAFT). The compressibility factor and radial distribution function of square-well monomer are obtained from Monte Carlo simulations. These results are correlated using density expansion. In developing the equation of state the exact analytical expressions are adopted for the second and third virial coefficients for the compressibility factor and the first two terms of the radial distribution function, while the higher order coefficients are determined from regression using the simulation data. In the limit of infinite temperature, the present equation of state and the expression for the radial distribution function are represented by the Carnahan-Starling equation of state. This semi-empirical equation of state gives at least comparable accuracy with other empirical equation of state for the square-well monomer fluid. With the new SAFT equation of state from the accurate expressions for the monomer reference and covalent terms, we compare the prediction of the equation of state to the simulation results for the compressibility factor and radial distribution function of the square-well monomer and chain fluids. The predicted compressibility factors for square well chains are found to be in a good agreement with simulation data. The high accuracy of the present equation of state is ascribed to the fact that rigorous simulation results for the reference fluid are used, especially at low temperatures and low densities.

Key words: Association, Equation of State, Monte Carlo, SAFT, Square-well

INTRODUCTION

The thermodynamic properties of chain fluids are of interest in theory and for industrial applications. A number of theories have appeared in literature to predict the properties for model chain fluids. Dickman and Hall [Dickman and Hall, 1986, 1988] and Honnell and Hall [Honnell et al., 1987, 1989] developed theories for the freely jointed hard-sphere chain fluid by extending Flory's probabilistic assumptions about lattice chains to continuous space. Using the concept of excluding volume and insertion probability of a chain molecule, they derived the generalized Flory (GF), the generalized Flory-Huggins (GFH), and the generalized Flory-Dimer (GFD) equations of state for the hard-sphere chain fluids. Using thermodynamic perturbation theory of polymerization (TPT), Wertheim developed an equation of state for the freely jointed hard-sphere fluid [Wertheim, 1984a, b, 1986a, b]. In TPT, the Helmholtz free energy of the polymer fluid is related to the Helmholtz free energy and the pair correlation function of the monomer fluid at the same reduced density and temperature. Chapman et al. [Chapman, 1990; Ghonasgi and Chapman, 1994] extended Wertheim's theory to mixtures. They developed the statistical associating fluid theory (SAFT) equation of state for the real fluids based on the Wertheim's theory. Chang and Sandler developed TPT-Dimer theory for hard chain fluids and found a good agreement between theory and simulation [Chang and Sandler, 1994, 1995]. Yethiraj and Hall developed an equation of state for hard-core square-well chains using the mean-field approximation [Yethiraj and Hall, 1991]. Banaszak et al. used TPT1 theory to generate equations of state for freely jointed square-well chains [Banaszak et al., 1994]. Tavares et al. also developed a TPT-Dimer for the square-well chain fluid by incorporating structural information for the diatomic square-well fluid [Tavares et al., 1995]. The main objective of this work is to derive an equation of state for the freely jointed square-well chain fluid, based on Wertheim's thermodynamic perturbation theory and rigorous simulation data. The NVT-Monte Carlo simulation is performed in order to obtain the equation of state of monomer fluid. We obtain the thermodynamic properties of square-well monomers directly from Monte Carlo (MC) simulations. The compressibility factors of chains fluids predicted by the present equation of state are compared with MC simulation results.

MONTE CARLO SIMULATION

The NVT-MC simulations for square-well monomers were performed to obtain the radial distribution functions and compressibility factors. In MC simulations for the bulk phase of square-well monomers we used the Metropolis algorithm, for a wide range of reduced densities ranging from 0.025 to 0.9 and temperatures ranging from 0.9 to 2.5. The number of molecules used in the simulations is 512. Periodic boundary conditions, using the minimum image convention, were applied in all

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the directions. In order to speed up the simulation, the linked list method was used [Allen and Tildesley, 1987]. A typical run is consisted of 30,000 equilibration cycles, followed by 90,000 production cycles. The results of the MC simulation for the square-well monomer are presented in Table 1.

Table 1. The MC simulation results for the compressibility factor and the contact values of the radial distribution function for the square-well monomer fluids at T^*=0.9, 1.0, 1.115, 1.333 and 2.5. The errors are the standard deviations in last digits estimated from four independent simulation runs (N=512, N_{avg}=120,000)

T^*	ρ^*	Z^M	g^M
0.9	0.025	0.795(5)	3.519(48)
	0.10	0.158(26)	8.713(346)
	0.70	0.770(8)	2.532(6)
	0.75	1.019(9)	2.940(14)
	0.80	2.303(16)	3.485(9)
	0.90	5.879(20)	4.960(14)
1.0	0.025	0.838(3)	2.913(21)
	0.05	0.670(6)	3.222(30)
	0.10	0.320(12)	5.769(44)
	0.15	0.173(14)	5.103(308)
	0.20	0.089(13)	4.385(125)
	0.25	0.012(20)	3.781(135)
	0.65	0.015(17)	2.307(7)
	0.70	0.629(8)	2.589(5)
	0.75	1.563(22)	2.998(8)
	0.80	2.801(19)	3.509(14)
	0.90	6.314(26)	4.940(28)
1.15	0.025	0.881(2)	2.437(22)
	0.05	0.770(3)	2.512(13)
	0.10	0.694(2)	2.165(10)
	0.15	0.394(8)	2.766(73)
	0.20	0.282(6)	2.725(49)
	0.25	0.200(9)	2.613(66)
	0.30	0.153(13)	2.481(51)
	0.35	0.103(8)	2.315(47)
	0.40	0.063(13)	2.190(16)
	0.45	0.030(7)	2.096(13)
	0.50	0.022(10)	2.050(12)
	0.55	0.085(7)	2.081(2)
	0.60	0.274(11)	2.183(8)
	0.65	0.641(13)	2.371(6)
	0.70	1.269(9)	2.662(8)
	0.75	2.175(12)	3.051(5)
	0.80	3.398(23)	3.560(9)
	0.90	6.850(30)	4.937(21)
1.333	0.025	0.917(2)	2.130(23)
	0.05	0.835(4)	2.147(15)
	0.10	0.690(3)	2.153(15)
	0.15	0.574(7)	2.137(20)
	0.20	0.484(5)	2.109(17)
	0.25	0.418(11)	2.061(9)
	0.30	0.371(8)	2.018(12)
	0.35	0.340(1)	1.975(8)
	0.40	0.328(4)	1.960(9)
	0.45	0.339(17)	1.965(6)
	0.50	0.394(12)	2.000(4)
	0.55	0.539(9)	2.085(5)
	0.60	0.791(8)	2.218(1)
	0.65	1.219(1)	2.437(4)
	0.70	1.860(10)	2.725(4)
	0.75	2.760(5)	3.109(6)
	0.80	3.945(27)	3.595(8)
	0.90	7.336(43)	4.941(29)
2.5	0.025	0.993(1)	1.490(4)
	0.05	0.987(2)	1.503(11)
	0.10	0.977(6)	1.517(8)
	0.15	0.979(4)	1.543(3)
	0.20	0.998(7)	1.566(3)
	0.25	1.037(3)	1.605(4)
	0.30	1.090(10)	1.653(4)
	0.35	1.178(2)	1.720(2)
	0.40	1.299(4)	1.800(6)
	0.45	1.461(5)	1.893(5)
	0.50	1.687(4)	2.024(5)
	0.55	1.987(7)	2.182(4)
	0.60	2.386(5)	2.379(4)
	0.65	2.936(5)	2.633(5)
	0.70	3.630(13)	2.938(10)
	0.75	4.528(12)	3.315(9)
	0.80	5.668(16)	3.776(6)
	0.90	8.820(25)	4.996(14)

EQUATION OF STATE FOR THE SQUARE-WELL MONOMER FLUID

The compressibility factor and the contact value of RDF of monomer fluid are obtained from MC simulation results in the literature and supplementary simulation results in this work. The simulation results are correlated using the density expansions:

$$Z^M=1+\sum_{i=1}^{9}B_{i+1}(T^*)\rho^{*i} \tag{1}$$

$$g^M=1+\sum_{i=0}^{4}g_i(T^*)\rho^{*i} \tag{2}$$

where $T^*(=kT/\varepsilon)$, $\rho^*(=\rho\sigma^3)$ are reduced temperature and density, respectively. In Eqs. (1) and (2), the exact analytical expressions are adopted for the second and third virial coefficients for the compressibility factor and the first two terms of the radial distribution function,

$$B_2(T^*)=b_0[1-(\lambda^3-1)\Delta] \tag{3}$$

$$\begin{aligned}B_3(T^*)=\frac{1}{8}b_0^2[&5-(\lambda^6-18\lambda^4+32\lambda^3-15)\Delta\\&-(2\lambda^6-36\lambda^4+32\lambda^3+18\lambda^2-16)\Delta^2\\&-(6\lambda^6-18\lambda^4+18\lambda^2-6)\Delta^3]\end{aligned} \tag{4}$$

Table 2. The fitted parameters for density expansion for the contact values RDF of square-well monomer fluids

i	g_{i1}	g_{i2}	g_{i3}
2	−2.08641	4.24608	−7.79942
3	2.42691	−5.46389	8.51813
4	0.46644	3.27859	−3.47026

$^{*}g_i=\sum_{k=1}^{3}g_{ik}(T^*)\Delta^k$ (i=2, 3, 4)

Table 3. The fitted parameters for density expansion for higher order virial coefficients of square-well monomer fluids

i	a_{i1}	a_{i2}	a_{i3}
4	−4.63192	−9.38959	18.68150
5	8.75256	−22.76898	−18.91511
6	17.03459	8.05376	−2.72835
7	−3.22009	20.43658	11.30432
8	−22.03529	6.59061	7.42395
9	12.07164	−15.20581	−10.55146

$^{*}B_i=\sum_{k=1}^{3}a_{ik}(T^*)\Delta^k$ (i=4, 5, 6, 7, 8, 9)

$$b_0=\frac{2}{3}\pi,\ \Delta=\exp(1/T^*)-1,\ \lambda=1.5$$

$$g_0=\Delta+1 \tag{5}$$

$$g_1=\pi(\Delta+1)\left[\frac{5}{12}+\left\{\left(\frac{1}{2}\lambda^4-\frac{4}{3}\lambda^3+\frac{5}{6}\right)\Delta\right\}+\frac{1}{2}(\lambda^2-1)^2\Delta^2\right] \tag{6}$$

Higher order coefficients are determined from the regression of the simulation data. In the limit of infinite temperature, this equation of state and expression for the radial distribution function are reduced to the Carnahan-Starling equation of state [Carnahan and Starling, 1969]. The values of the high-order parameters in equations are defined and summarized in Tables 2 and 3.

EQUATION OF STATE FOR THE SQUARE-WELL CHAIN FLUID

We consider a SAFT form of equation of state [Chapman, 1990; Ghonasgi and Chapman, 1994] for homonuclear freely jointed tangent square-well chain fluids. The equation of state of an associating fluid mixture can be written as a sum of separate contributions. The corresponding Helmholtz free energy is given by

$$\frac{A}{NkT}=\frac{A^{ideal}}{NkT}+\frac{A_R^{mono}}{NkT}+\frac{A^{chain}}{NkT}+\frac{A^{assoc}}{NkT} \tag{7}$$

where N is the number of monomers, T is the temperature, k is the Boltzman constant. A_R^{mono} is the Helmholtz free energy of the monomer reference fluid. Similarly, the compressibility factor can also be expressed as a sum of the square-well monomer, chain, and association contributions.

A^{ideal} and A^{assoc} are given by

$$\frac{A^{ideal}}{NkT}=\ln(\rho\Lambda^3)-1 \tag{8}$$

$$\frac{A^{assoc}}{NkT}=\sum_{a=1}\left(\ln X_a-\frac{X_a}{2}\right)+\frac{s}{2} \tag{9}$$

where ρ is the total number density of monomer segments, X_a is the fraction of monomers, s is the number of associating sites on each segment. The fraction of monomers is obtained from

$$X_a=\frac{1}{1+\sum_{b=1}^{s}\rho X_b\Delta_{ab}} \tag{10}$$

where the covolume Δ_{ab} is defined as

$$\Delta_{ab}=K_{ab}f_{ab}g^M(\sigma) \tag{11}$$

$$f_{ab}=\exp(-\psi_{ab}/kT)-1 \tag{12}$$

Here $g^M(\sigma)$ is the pair correlation function of the reference fluid, and σ is the bond length of this model, ψ_{ab} is the association potential. The covalent contribution A^{chain} is given by

$$\frac{A^{chain}}{NkT}=-(m-1)\ln y^M(\sigma) \tag{13}$$

where m is the number of segments in a chain, and $y^M(\sigma)$ is the cavity correlation function evaluated at the bond length σ. The compressibility factor of the square-well chain fluids is obtained by differentiating the Helmholtz free energy (7) with respect to volume.

$$Z=\eta\frac{\partial}{\partial\eta}\left(\frac{A}{NkT}\right) \tag{14}$$

$$Z=mZ^M-(m-1)Z_{chain}+Z_{assoc} \tag{15}$$

$$Z_{chain}=\eta\frac{\partial}{\partial\eta}[g^M(\sigma)] \tag{16}$$

$$Z_{assoc}=\sum_{a=1}\eta\left[\left(\frac{\partial X_a}{\partial\eta}\right)_{T,N}\left(\frac{1}{X_a}-\frac{1}{2}\right)\right] \tag{17}$$

RESULTS AND DISCUSSION

The NVT-MC simulations for square-well monomers were performed to supplement the previous simulation data especially at low temperatures. Fig. 1 shows the compressibility factor of square-well monomer fluid at T^*=1.15, 1.333, 1.5, 2.0, 2.5 and 3.0. The symbols are the simulation data of Tavares et al. and this work. A comparison between literature and the present simulation data tests the consistency of our MC simulation code as shown in Fig. 1.

In order to obtain the equation of state of chain fluids, Banaszak et al. [Banaszak et al., 1994] used the Barker-Henderson perturbation theory to estimate the compressibility factor and radial distribution function (RDF) at contact for the square-well monomer. In this work, the equation of state of chain fluids is developed by using the compressibility factor and radial distribution function of square-well monomer which are obtained from rigorous simulation data. We compare simulation results for the compressibility factor and radial distribution function of the square-well monomer and the compressibility factor of the square-well chain fluid with the predictions of the Banaszak et al.'s and the equation of state in this work. Figs. 2 and 3 show the compressibility factor of square-well monomer fluid at T^*=1.0, 1.15, 1.333, 1.5, 2.0, 2.5, 3.0 and 4.0 and Figs. 4 and 5 show the contact values of radial distribution function of square-well monomer at T^*=1.0, 1.15, 1.333, 1.5, 2.0, 2.5, 3.0 and 4.0. The symbols represent the simulation data of Tavares et al. and this work and the curves represent the predictions of the theories. In Figs. 2 and 4 the symbols represent the simulation results in the literature. In Figs. 3 and 5 the symbols represent the simulation results in this work. In Figs. 2 and 3 are shown the predictions of the Banaszak et al.'s and the present theory and Monte Carlo results for the compressibility factors of the square-well monomer fluids. The present equation of state gives accurate predictions at high densities and low temperatures. In Figs. 4 and 5 are shown the predictions of the Banaszak et al.'s and the present theory and Monte Carlo results for the radial distribution function of square-well monomer. Especially the results of the present theory for the contact values RDF of square-well monomer fluids agree with MC simulations better than Banaszak et al.'s at low densities and low temperatures because the exact analytical expressions are adopted for the first two terms of the density expansion for the radial distribution function.

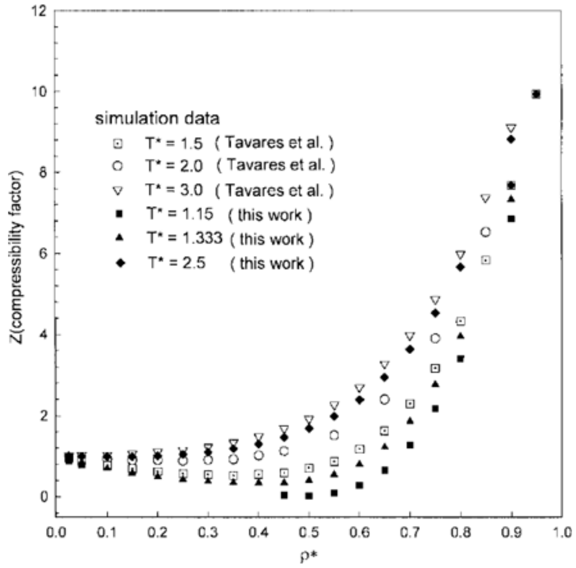

Fig. 1. The compressibility factor of square-well monomer fluid at T^*=1.15, 1.333, 1.5, 2.0, 2.5, 3.0. The symbols are the simulation data of Tavares et al. [1995] (grey symbols) and this work (solid symbols).

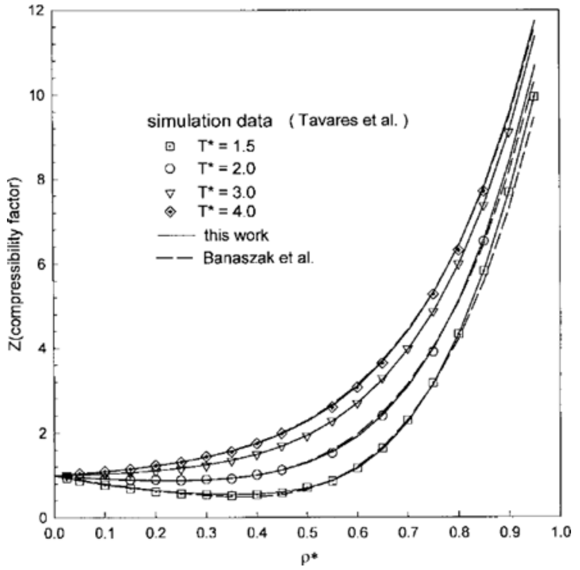

Fig. 2. The compressibility factor of square-well monomer fluid at T^*=1.5, 2.0, 3.0, 4.0. The symbols are the simulation data of Tavares et al. [1995].

Figs. 6 and 7 show the compressibility factor of square-well chain fluid at T^*=1.5, 2.0, 3.0 and 4.0 and the results for the

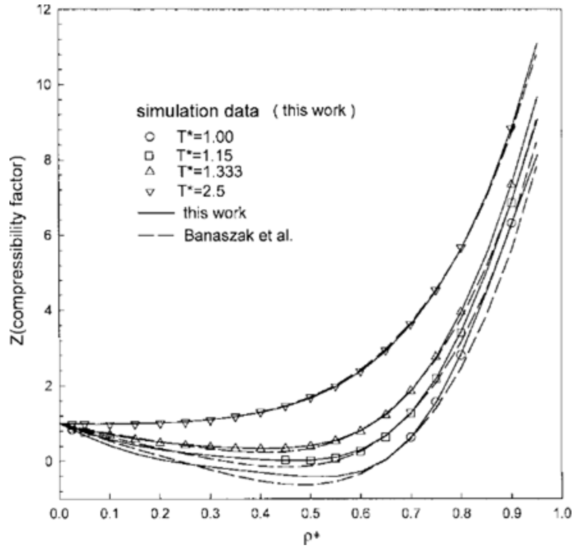

Fig. 3. The compressibility factor of square-well monomer at T^*=1.0, 1.15, 1.333, 2.5. The symbols are the simulation data in this work.

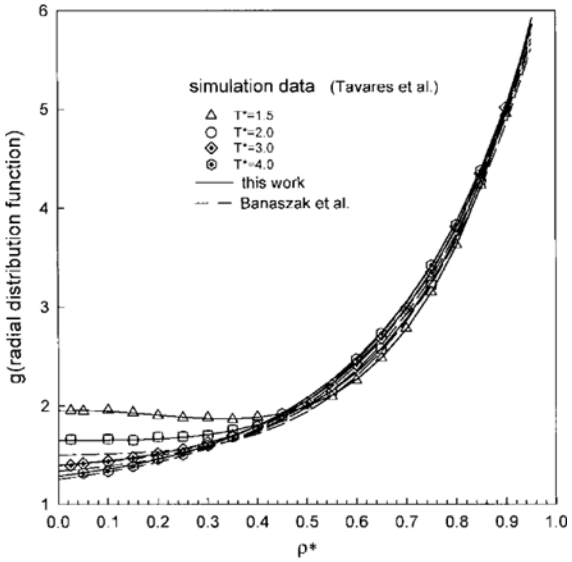

Fig. 4. The contact values of radial distribution function of square-well monomer at T^*=1.5, 2.0, 3.0, 4.0. The symbols represent the simulation data Tavares et al. [1995].

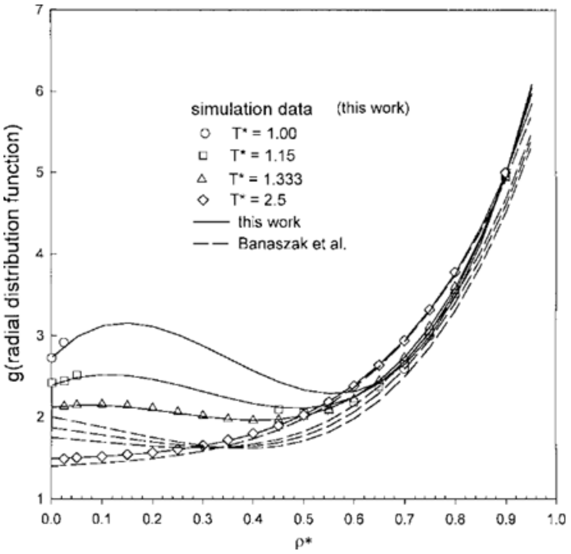

Fig. 5. The contact values of radial distribution function of square-well monomer at T^*=1.0, 1.15, 1.333, 2.5. The symbols represent the simulation data in this work.

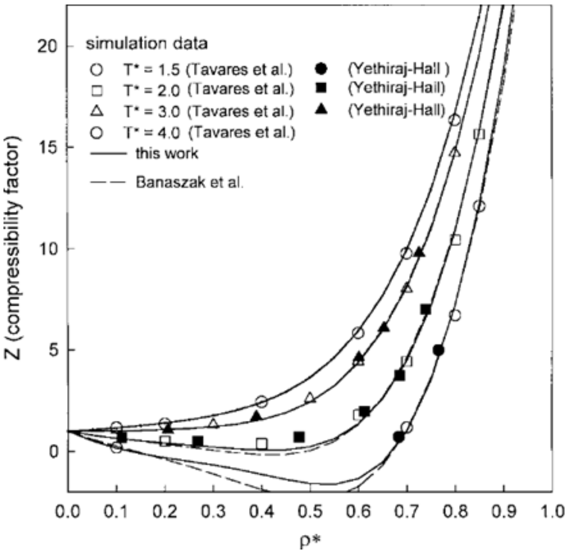

Fig. 6. The compressibility factor of square-well 4-mer fluid at T^*=1.5, 2.0, 3.0, 4.0. The symbols are the simulation data Tavares et al. [1995] (grey symbols) and Yethiraj and Hall [1991] (solid symbols).

square-well chain fluid are compared with simulation results of 4-mers and 16-mers. A good agreement between the present theory and simulations are found as shown in Figs. 6 and 7. For monomer fluids the predictions of the perturbation theory of the Banaszak et al.'s and the present theory show the considerable difference at low temperatures. But the difference isn't nearly represent in Figs. 6 and 7 because this does not lead to a significant difference for the compressibility factor of chain fluids because the errors are attenuated by taking the logarithm of the radial distribution function of monomer reference fluid as in the Eq. (13). In Figs. 3, 6 and 7, the region of the negative compressibility factors represents a metastable region. More accurate information of the metastable region will be gained from a Gibbs Ensemble Monte Carlo simulation (GEMC).

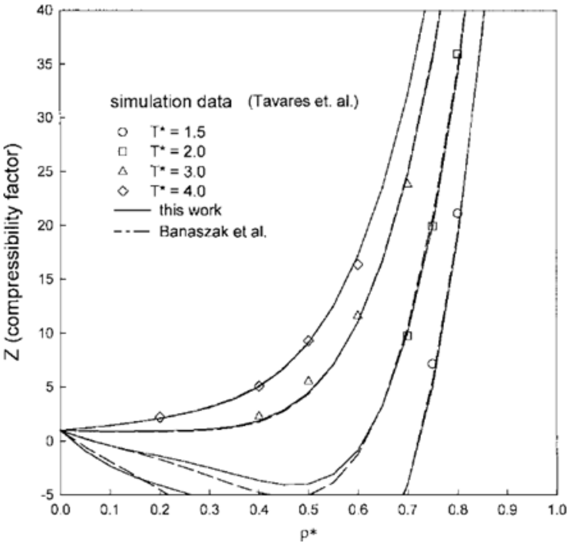

Fig. 7. The compressibility factor of square-well 16-mer at T^*= 1.5, 2.0, 3.0, 4.0. The symbols are the simulation data Tavares et al. [1995].

CONCLUSIONS

NVT-MC simulations for the square well monomer fluid are performed to obtain the compressibility factor and the contact values of the radial distribution function. Using MC simulation results for the compressibility factor of square-well monomer fluid and the radial distribution function, we developed an equation of state for the freely jointed square-well chain fluid. The predictions of the compressibility factor of the square-well chain fluid from the present theory are compared with simulation results of the literature and this work. A good agreement between the present theory and simulation results is found.

NOMENCLATURE

A : Helmholtz free energy of the reference fluid
A^{assoc} : associating Helmholtz free energy
A^{chain} : chain Helmholtz free energy
A^{ideal} : Helmholtz free energy of ideal state
A_R^{mono} : Helmholtz free energy of the reference fluid
B_2, B_3: second and third virial coefficients for the compressibility factor
f_{ab} : mayer function
$g^M(\sigma)$: reference fluid pair correlation function
k : Boltzmann's constant
m : number of segments in a chain
N : number of monomers
T, T^* : temperature, reduced temperature
s : number of associating sites
X_a : fraction of monomers
$y^M(\sigma)$: cavity correlation function evaluated at the bond length σ
Z^M : reference fluid compressibility factor

Greek Letters

ρ, ρ^* : total number density of monomer segments, reduced density
ψ_{ab} : the association potential

Superscripts

assoc : association
ideal : ideal gas
chain : chain term
M : monomer
$*$: reduced units

Subscript

a, b : associating sites

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