Calculating thermodynamic properties from perturbation theory
Part III. The mixtures of square-well chain fluid

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Abstract
A completely analytic perturbation theory has been developed to calculate the Helmholtz energy, compressibility factor, internal energy and constant-volume heat capacity for square-well chain fluid mixtures. This theory is based on the improved Barker–Henderson macroscopic compressibility (mc) approximation proposed by Zhang, the first-order perturbation theory of Wertheim in which Zhang’s analytic monomer radial distribution function as the function of temperature and monomer density is used, and a simple mixing rule similar to that of Hino–Prausnitz. The validity of the perturbation theory is evaluated by comparing the calculated compressibility factor, internal energy and constant-volume heat capacity for the freely jointed square-well chain mixtures from the theory to MC simulation data. The results show that the theory predicts results in good agreement with simulation results.

Keywords: Perturbation theory; Mixture; Heat capacity; Equations of state

1. Introduction
Analytic representations derived from perturbation theories have become very popular in understanding and calculating the thermodynamic properties of chain-like fluids due to their simplicity and ability to describe wide range of components and conditions. Lots of work over the years focus on perturbed hard-sphere chain (PHSC) equations of state (EOS), which are capable of correlating the thermodynamic properties of small molecules as well as those of chain-like molecules. In most of these works, such as the PHSC EOS for normal fluids and polymers by Hino and Prausnitz [1], the square-well EOS for chain molecules by Sadowski [2] and the EOS for square-well diatomic fluids and fluid mixtures by Gulati and Hall [3], the Barker–Henderson second-order expansion [4,5] was used.

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On the basis of the Barker–Henderson macroscopic compressibility (mc) approximation, an improved second-order and higher-order term is proposed in our previous paper [6] by assuming that the numbers of molecules in every two neighbor shells are correlated. Based upon the improvement, analytic representations of the square-well potential hard-sphere perturbation theory [7] and the square-well chain fluid perturbation theory [8] are derived. These models lead to good predictions of the compressibility factor, as well as the residual internal energy and the constant-volume heat capacity. In this paper, the perturbation theory is extended to fluid mixtures containing small molecules and chain-like molecules using a simple mixing rule similar to that of Hino–Prausnitz [1].

2. Theoretical

For a one-component system formed by $N$ spherical molecules in a volume $V$ at a temperature $T$, Barker and Henderson [4] imagined that the range of intermolecular distances $r$ is divided into intervals $(r_0, r_1)$, $(r_1, r_2)$, . . . $(r_i, r_{i+1})$, . . . etc. and assumed that perturbation pair interactions $u_p(r_i)$ could be regarded as having a constant value $u_i$ in a spherical shell of interval $(r_i, r_{i+1})$ surrounding central molecules and that the numbers of molecules $N_i$ in different shells would be irrelevant. An approximate expression of the second-order perturbation term by the so-called mc or local compressibility (lc) approximation can be derived. As Barker and Henderson [5] realized, in the mc approximation there is a problem in that by taking the limit as the interval width $(r_i, r_{i+1})$ tends to zero, the shells are not large macroscopic volumes. Therefore, Zhang [6] assumed that the numbers of molecules in every two neighboring shells are correlated, and the correlation coefficient $\phi$ of the numbers of molecules in every two neighboring shells is in direct proportion to the product of the particle density $\rho$ and the hard volumes $\pi \sigma^3 / 6$ of molecules in this two neighboring shells:

$$\phi = \frac{\langle N_i N_{i+1} \rangle - \langle N_i \rangle \langle N_{i+1} \rangle}{\sqrt{\langle N_i^2 \rangle - \langle N_i \rangle^2} \sqrt{\langle N_{i+1}^2 \rangle - \langle N_{i+1} \rangle^2}} = K \rho^2 \left( \frac{\pi}{6} \sigma^3 \right)^2 = K \eta^2$$

where $\eta = \pi \rho \sigma^3 / 6$, $K$ is a proportionate coefficient. From Zhang’s work, when the fluid has condensed (in this condition $\eta_{\text{con}} = 0.493$ [9]), $\phi_{\text{con}} = 1$. So $K \approx 1/\eta_{\text{con}}^2$.

With a derivation similar to that of Barker and Henderson [4], a little more complex perturbation expansion of the Helmholtz energy for a system of the one-component spherical molecules have been obtained by Zhang [7]

$$\frac{A - A_0}{NkT} = \left( \frac{A_1}{NkT} \right) + \left( \frac{A_2}{NkT} \right) + O(\beta^3)$$

and

$$\frac{A_1}{NkT} = 2\pi \rho \delta \int_0^\infty u_p(r)g_0(r)r^2 dr$$

$$\frac{A_2}{NkT} = -\pi \rho \delta^2 (1 + 2K\eta^2) \left( \frac{\partial P}{\partial P} \right)_0 kT \int_0^\infty u_p^2(r)g_0(r)r^2 dr$$

where $A$ and $A_0$ are, respectively, the Helmholtz energy of the studied and the reference fluid. $A_1$ and $A_2$ are the first- and second-order perturbation terms, and $g_0(r)$ and $\left( \partial P/\partial P \right)_0$ are the radial distribution function
and the compressibility for the reference fluid, respectively. \( \beta = (kT)^{-1} \), where \( k \) is the Boltzmann constant. Eq. (4) is better than that of the original mc approximation, especially at intermediate and high densities, when compared with simulation data [6,7].

Considering a chain molecular fluid consisting of \( m \) segments (monomers) per chain molecule, the Helmholtz energy for the chain molecules in excess of that for the reference state at the same temperature and the monomer packing fraction \( \eta \) can be expressed as

\[
\frac{A - A_0}{NkT}_{\text{chain}} = \left( \frac{A - A_0}{NkT} \right)_{\text{mono}} + \left( \frac{A - A_0}{NkT} \right)_{\text{pert}}
\]

(5)

Here subscript “pert” indicates the term which represents the excess Helmholtz energy term due to the bond constraints between segments, “chain” and “mono” indicate chain and monomer fluids, respectively. The analytic perturbation theory, Eqs. (1)–(3), derived previously is used here to calculate thermodynamic properties of the monomer.

\[
\frac{A - A_0}{NkT}_{\text{mono}} = m \left( \frac{A - A_0}{NkT} \right)_{\text{m=1}}
\]

(6)

where subscript “m = 1” indicates one-component spherical molecules.

In order to extend the perturbation theory to mixtures, a square-well site-site pair potential energy is given by

\[
u_{ij}(r_{ij}) = \begin{cases} 
\infty & r_{ij} < \sigma_{ij} \\
-e_{ij} & \sigma_{ij} \leq r_{ij} < \lambda \sigma_{ij} \\
0 & r_{ij} \geq \lambda \sigma_{ij}
\end{cases}
\]

(7)

where \( r_{ij} \) is the internomomer distance, \( \sigma_{ij} \) the hard core diameter, \( e_{ij} \) the well depth, \( \lambda \) the well width, \( \sigma_{ij} \) and \( e_{ij} \) are defined by using conventional combining rules for interactions between a pairs of unlike monomers

\[
\sigma_q = \frac{1}{2}(\sigma_i + \sigma_j)
\]

(8)

\[
e_q = \sqrt{e_i e_j} \]

(9)

The mixing rules for the parameters for a mixture of \( M \) components of Hino and Prausnitz [1] are used:

\[
\langle m^2 \sigma^2 > = \sum_{i=1}^{M} \sum_{j=1}^{M} x_i x_j m_i m_j \sigma_q^2 e_{ij}
\]

(10)

\[
\langle m^2 \sigma^2 \rangle = \sum_{i=1}^{M} \sum_{j=1}^{M} x_i x_j m_i m_j \sigma_q^2 e_{ij}
\]

(11)

where the angular bracket denotes an average property of the mixture, \( x_i \) is the mole fraction of component \( i \).
Applying these mixing rules to Eqs. (2) and (3), leads to the following first- and second-order perturbation terms of the Helmholtz energy

\[
\frac{A_1}{NkT} = -2\pi \rho \beta \sum_{i=1}^{M} \sum_{j=1}^{M} x_i x_j m_i m_j \sigma_{ij}^3 \int_{0}^{\lambda} g_0(R) R^2 dR
\]

(12)

\[
\frac{A_2}{NkT} = -\pi \rho \beta^2 (1 + 2K\eta^2) \sum_{i=1}^{M} \sum_{j=1}^{M} x_i x_j m_i m_j \sigma_{ij}^3 \varepsilon_{ij} \varepsilon_{ij} \frac{\partial \rho}{\partial P} \int_{0}^{\lambda} g_0(R) R^2 dR
\]

(13)

where \( R = r/\sigma \). The packing fraction \( \eta \) of the mixture is given by

\[
\eta = \frac{\pi \rho}{6} \sum_{i=1}^{M} x_i m_i \sigma_{ii}^3
\]

(14)

and

\[
D = \left( \sum_{i=1}^{M} x_i m_i \sigma_{ii}^3 \right)^{-1}
\]

(15)

For the higher-order perturbation terms \( i > 2 \), another approximation given by Barker and Henderson [5] is used

\[
A_i = A_1 \left( \frac{2A_2}{A_1} \right)^{i-1} \quad (i > 2)
\]

(16)

Substituting Eqs. (12) and (13) into Eqs. (16) and (6), with a similar process to that of Zhang [7,8], leads to

\[
\left( \frac{A - A_0}{NkT} \right)_{\text{mono}} = -12D_0 \sum_{i=1}^{M} \sum_{j=1}^{M} x_i x_j m_i m_j \sigma_{ij}^3 \left[ \exp \left( \frac{\beta \varepsilon_{ij}}{\alpha} \right) - 1 \right] \sum_{j=1}^{\infty} C_i \left( \frac{\eta}{1 - \eta} \right)^j
\]

(17)

where \( \alpha \) is the correction factor defined by Zhang [7,8] to improve Barker and Henderson’s mc approximation [4]:

\[
\alpha = \frac{\beta}{(1 + 2K\eta^2)} \left( \frac{\partial P}{\partial \rho} \right)_{\text{ref}}
\]

(18)

When the Carnahan–Starling hard-sphere equation [10] is used as reference fluid, \( \alpha \) can be obtained from Eq. (18):

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

(19)

Parameter \( C_i \) in Eq. (17) is defined as [7,8]

\[
C_i = \int_{0}^{\lambda} g_0(R) R^2 dR
\]

(20)
here $g_0(I = 1, 2, 3, \ldots)$ are the truncated coefficients of the radial distribution function for the reference hard-sphere fluid.

$$g_0(R) = \sum_{I=1}^{\infty} C_I \left( \frac{\eta}{1-\eta} \right)^I$$

(21)

and the coefficients of the first four terms are

$$
\begin{align*}
\bar{g}_0 &= 1 \\
\bar{g}_2 &= 7 - 6R + 0.5R^3, \quad R < 2 \\
\bar{g}_3 &= 21.019724 - 60.405915R^{-1} + 39.886191R^{-2}, \quad R < 2 \\
\bar{g}_4 &= -9.100022 + 13.683797R - 4.58675R^2, \quad R < 2
\end{align*}
$$

(22)

According to the Wertheim first-order thermodynamic perturbation theory (TPT1) for chain molecules [11] and extending this theory to mixtures, the total contribution of bond formation in a chain molecule mixture is summed over all the components as follows

$$\left( \frac{A - A_0}{NkT} \right)_{\text{pert}} = -\sum_{i=1}^{M} x_i (m_i - 1) [\ln g^{\text{SW}}(\eta, \beta \epsilon) - \ln g^{\text{SW}}(\eta \rightarrow 0, \beta \epsilon)]$$

(23)

where the term $g^{\text{SW}}$ is the limiting value of the radial distribution function of square-well monomers (SWS) at the segments contact point $\sigma^+_i$ when approached from infinite site–site separation distance. $g^{\text{SW}}$, as function of temperature and monomer density, has been expressed similarly as in Eq. (17) by Zhang [8].

$$g^{\text{SW}}(\eta, \beta \epsilon) = \left( \frac{\eta}{1-\eta} \right)^j$$

(24)

and

$$g^{\text{SW}}(\eta \rightarrow 0, \beta \epsilon) = \sum_{i=0}^{4} a_i (\beta \epsilon)^i$$

(25)

where the parameters $a_i$ have been evaluated with the Monte Carlo (MC) simulation results [8, 12] over the range $0 \leq \beta \epsilon \leq 0.7$ and $0 \leq \eta \leq 0.5$, and their value is listed in Table 1.

<table>
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<tr>
<th>$i$</th>
<th>1</th>
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<th>3</th>
<th>4</th>
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<tr>
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<tr>
<td>4</td>
<td>-23.186</td>
<td>68.17</td>
<td>-37.694</td>
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</tr>
</tbody>
</table>
When Eqs. (23) and (17) are substituted into Eq. (5), this leads to an analytic expression for the Helmholtz energy of the square-well chain mixtures.

By usual derivations, one obtains the analytical expressions for other thermodynamic properties, which are as follows.

1. Compressibility factor:

$$Z_{\text{chain}} - Z_0 = \eta \frac{\partial}{\partial \eta} \left( \frac{A - A_0}{NkT} \right)_{\text{chain}}$$

(26)

Here a compressibility factor for reference fluid similar to that of Chiew for the athermal hard-sphere chain mixtures [13] is used.

$$Z_0 = 1 + 4Dn \sum_{i=1}^{M} \sum_{j=1}^{M} x_i m_i s_j m_j \sigma_{ij}^3 g_{ij}(\sigma_{ij}^+, \eta)$$

(27)

where $g_{ij}$, the radial distribution function for a mixture at contact prior to bonding, is given by a similar form of Boublik–Mansoori extension of Carnahan–Starling hard sphere equation [14,15].

$$g_{ij}(\sigma_{ij}^+, \eta) = \frac{1}{1 - \eta + \frac{3}{2} (1 - \eta)^2 + \frac{1}{2} (1 - \eta)^3}$$

(28)

and

$$\xi_{ij} = Dn \left( \frac{\sigma_{ij}^+}{\sigma_0} \right) \sum_{I=1}^{M} x_I m_I \sigma_{II}^3$$

(29)

by substituting Eqs. (17) and (23) into Eq. (5), then into Eq. (26), the compressibility factor for the square-well chain fluid mixtures can be derived as

$$Z_{\text{chain}} = Z_{\text{mono}} + Z_{\text{pert}} + Z_0$$

(30)

where

$$Z_{\text{mono}} = -12Dn \sum_{i=1}^{M} \sum_{j=1}^{M} x_i m_i s_j m_j \sigma_{ij}^3 \left[ \frac{\partial}{\partial \eta} \left( \frac{N \sum_{I=1}^{M} C_I \left( \frac{\eta}{1 - \eta} \right)^I}{\eta} \right) \left[ \exp \left( \frac{\beta \varepsilon_{ij}}{\alpha} \right) - 1 \right] \right]$$

(31)

$$Z_{\text{pert}} = -\sum_{i=1}^{M} x_i (m_i - 1) \left[ \frac{\partial}{\partial \eta} g_{SWS}(\eta, \beta \varepsilon_{ii}) \right]$$

(32)

2. Internal energy ($U$)

$$\left( \frac{U - U_0}{NkT} \right)_{\text{chain}} = \beta \frac{\partial}{\partial \beta} \left( \frac{A - A_0}{NkT} \right)_{\text{chain}} = \left( \frac{U - U_0}{NkT} \right)_{\text{mono}} + \left( \frac{U - U_0}{NkT} \right)_{\text{pert}}$$

(33)
\[ (U - U_0)_{\text{mono}} = -12D \sum_{i=1}^{M} \sum_{j=1}^{M} x_i x_j m_i m_j \sigma_{ij}^0 \left[ \beta x_i \exp \left( \frac{\beta x_i}{\alpha} \right) \sum_{i=1}^{\infty} C_i \left( \frac{\eta}{1 - \eta} \right)^i \right] \]  

\[ (U - U_0)_{\text{pert}} = -\sum_{i=1}^{M} x_i (m_i - 1) \left\{ \frac{\beta \left[ \ln g_{\text{SWS}}(\eta, \beta \varepsilon_{ii}) - \ln g_{\text{SWS}}(\eta \rightarrow 0, \beta \varepsilon_{ii}) \right]}{\partial (\ln \beta)} \right\} \]  

3. Constant-volume heat capacity \((C_V)\)

\[ \frac{C_V}{Nk} = -\beta^2 \frac{\partial^2}{\partial \beta^2} \left( A - A_0 \right)_{\text{chain}} = \frac{C_V}{Nk}_{\text{mono}} + \frac{C_V}{Nk}_{\text{pert}} \]  

Here

\[ \frac{C_V}{Nk}_{\text{mono}} = 12D \sum_{i=1}^{M} \sum_{j=1}^{M} x_i x_j m_i m_j \sigma_{ij}^0 \left[ \beta x_i \exp \left( \frac{\beta x_i}{\alpha} \right) \sum_{i=1}^{\infty} C_i \left( \frac{\eta}{1 - \eta} \right)^i \right] \]  

\[ \frac{C_V}{Nk}_{\text{pert}} = -\sum_{i=1}^{M} x_i (m_i - 1) \left\{ \frac{\beta \left[ \ln g_{\text{SWS}}(\eta, \beta \varepsilon_{ii}) - \ln g_{\text{SWS}}(\eta \rightarrow 0, \beta \varepsilon_{ii}) \right]}{\partial (\ln \beta)} \right\} \]  

3. Results and discussion

In this section, comparisons are made between the thermodynamic properties calculated from the proposed theory and the results from MC simulations. In order to be consistent with the bulk of the theoretical work and simulation work available for square-well fluids mixtures, we consider a mixture which consists of freely jointed square-well chain molecules with well width \(\lambda = 1.5\).

Fig. 1 shows the predictions of compressibility factors from Eqs. (30), (27), (31) and (32) for the square-well 1-mer and dimer–monomer mixtures, and compares the results with those of discontinuous canonical molecular dynamics (DCMD) simulations by Gulati and Hall [3], where \(x_2 = 1/3\). Reduced hard-sphere diameter ratios are \(\sigma_2/\sigma_1 = 0.5\) and \(\sigma_2/\sigma_1 = 2\), reduced well depth ratios range from \(\varepsilon_2/\varepsilon_1 = 0.5\) to \(\varepsilon_2/\varepsilon_1 = 1.5\), and reduced temperatures are \(\beta \varepsilon_1 = 0.5\) and \(\beta \varepsilon_1 = 1/3\). The curves represent the predictions of our perturbation theory, and the symbols are DCMD simulation results [3]. Similarly, Fig. 2 shows the compressibility factors from our predictions and DCMD simulation results [3] for square-well dimer mixtures with \(x_1 = 0.5\), \(\beta \varepsilon_1 = 0.5\) and \(1/3\), \(\sigma_2/\sigma_1 = 1\) and 2, \(\varepsilon_2/\varepsilon_1 = 0.5\), 1 and 1.5.

Fig. 3 presents the predictions of reduced internal energy from Eqs. (33)–(35) for the square-well mixtures of 2- and 4-mer, and compares the results with the MC simulation results, for \(x_2 = 0.5\), \(\sigma_2/\sigma_1\) ranging from 0.5 to 1, \(\varepsilon_2/\varepsilon_1\) ranging from 0.5 to 1, and \(\beta \varepsilon_1\) ranging from 0.25 to 0.5. The curves represent the predictions of our perturbation theory, and the symbols are our MC simulation results.

The canonical ensemble MC simulations for freely-jointed tangent square-well chain mixtures are used to obtain the reduced internal energy and constant-volume heat capacity. A conventional \(NVT\) MC method similar to our previously works [8] is used. Chain molecules for the mixture were cast pre-rata in a cubic
Fig. 1. The compressibility factor of 1- and 2-mer mixtures ($m_1 = 1, m_2 = 2$) at $x_1 = 1/3$. The symbols are DCMD results by Gulati and Hall [3]. Curves represent the predictions of our perturbation theory.

Fig. 2. The compressibility factor for the square-well mixtures of 2-mer ($m_1 = m_2 = 2$) at $x_1 = 0.5$. The symbols are DCMD results [3]. Curves represent the predictions of our perturbation theory.
Fig. 3. The reduced internal energy for the square-well mixtures of 2- and 4-mer ($m_1 = 2, m_2 = 4$) at $x_1 = 0.5$. The symbols are our MC results. Curves represent the predictions of the perturbation theory.

box with periodic boundary condition, the number of chain molecules was fixed to be 256, and the border length of the cell box was adjusted according to density. An outer cycle takes place to move the mass center of a randomly selected molecule and many inner cycles are needed to settle each sphere of the chain molecule, the maximum size for each type of moving is adjusted to give a 50% acceptance ratio. Generally speaking, the system was first relaxed to equilibrium, requiring more than $2 \times 10^5$ outer cycles. After equilibrium, the thermodynamic properties were calculated using another more than $5 \times 10^5$ outer cycles. The simulation results are listed in Tables 2 and 3 in the Appendix A.

<table>
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<tr>
<th>$\sigma / \sigma_1$</th>
<th>$\xi / \xi_1$</th>
<th>$x_2$</th>
<th>$\eta$</th>
<th>$(U - U_0)/kT$</th>
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</thead>
<tbody>
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<td></td>
<td>$\beta \varepsilon = 0.5$</td>
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<td>0.367</td>
<td>$-5.42 \pm 0.54$</td>
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Table 3
Monte Carlo simulation results of constant-volume heat capacity for the square-well mixtures of 2- and 4-mer ($m_1 = 2, m_2 = 4$)

<table>
<thead>
<tr>
<th>$\sigma_2/\sigma_1$</th>
<th>$\sigma_2/\epsilon_1$</th>
<th>$x_2$</th>
<th>$\eta$</th>
<th>$C_V$</th>
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<td>$\beta \epsilon_1 = 0.5$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.5</td>
<td>0.209</td>
<td>0.804 ± 0.161</td>
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<tr>
<td></td>
<td>0.262</td>
<td>0.769 ± 0.132</td>
<td>0.307 ± 0.062</td>
<td>0.106 ± 0.022</td>
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<td>1</td>
<td>0.5</td>
<td>0.5</td>
<td>0.209</td>
<td>0.288 ± 0.058</td>
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<tr>
<td></td>
<td>0.262</td>
<td>0.281 ± 0.052</td>
<td>0.094 ± 0.018</td>
<td>0.0055 ± 0.017</td>
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<td>0.209</td>
<td>0.797 ± 0.133</td>
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<tr>
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<td>0.262</td>
<td>0.745 ± 0.149</td>
<td>0.296 ± 0.059</td>
<td>0.082 ± 0.021</td>
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In Fig. 4, the constant-volume heat capacity predicted from Eqs. (36)–(38) are compared with the MC results for the square-well mixtures of 2- and 4-mer at $x_2 = 0.5, \sigma_2/\sigma_1 = 0.5$ and 1, $\epsilon_2/\epsilon_1 = 0.5$ and 1. The curves represent the predictions of the perturbation theory, and the symbols are our MC simulation results.

In these figures, the predictions of the thermodynamic properties for the square-well chain mixtures agree well with the simulation results at intermediate to high densities and relative wide reduced temperatures.

Fig. 4. The reduced constant-volume heat capacity for the square-well mixtures of 2- and 4-mer ($m_1 = 2, m_2 = 4$) at $x_2 = 0.5$. The symbols are our MC results. Curves represent the predictions of the perturbation theory.
4. Conclusions

We have developed a completely analytic perturbation theory to calculate the Helmholtz energy, compressibility factor, internal energy and constant-volume heat capacity for the square-well chain fluid mixtures. This theory is based on the improved Barker–Henderson MC approximation of the second-order perturbation term proposed by Zhang [6–8], the first-order perturbation theory of Weitheim [11] in which an analytic radial distribution function of square-well monomers to form chains has been obtained by Zhang as the function of temperature and monomer density, and a simple mixing rule similar to that of Hino–Prausnitz [1]. The validity of the perturbation theory is evaluated by comparing the calculated compressibility factor, internal energy and constant-volume heat capacity for the freely jointed square-well chain mixtures from our theory to MC simulation data. The results show that the predicting results are reasonably well.

List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Helmholtz energy</td>
</tr>
<tr>
<td>$A_i$</td>
<td>$i$th-order perturbation term for the Helmholtz energy</td>
</tr>
<tr>
<td>$b$</td>
<td>equations of state parameter</td>
</tr>
<tr>
<td>$C_f$</td>
<td>coefficient in Eq. (17).</td>
</tr>
<tr>
<td>$C_V$</td>
<td>constant-volume heat capacity</td>
</tr>
<tr>
<td>$D$</td>
<td>coefficient in Eq. (14)</td>
</tr>
<tr>
<td>$g_0(r)$</td>
<td>radial distribution function of the reference system</td>
</tr>
<tr>
<td>$g(\eta, \beta \varepsilon)$</td>
<td>radial distribution function of hard spheres at contact</td>
</tr>
<tr>
<td>$\bar{g}_0$</td>
<td>the coefficient of Eq. (15) for $g_0(r)$</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$K$</td>
<td>proportion coefficient in Eq. (1)</td>
</tr>
<tr>
<td>$m$</td>
<td>number of hard spheres per molecule</td>
</tr>
<tr>
<td>$M$</td>
<td>number of components</td>
</tr>
<tr>
<td>$N$</td>
<td>total number of molecules</td>
</tr>
<tr>
<td>$N_i$</td>
<td>number of molecules in spherical shell $i$</td>
</tr>
<tr>
<td>$P$</td>
<td>pressure</td>
</tr>
<tr>
<td>$r$</td>
<td>distance of the interacting particles</td>
</tr>
<tr>
<td>$R$</td>
<td>reduced distance of interacting particles defined as $R = r/\sigma$</td>
</tr>
<tr>
<td>$T$</td>
<td>absolute temperature (K)</td>
</tr>
<tr>
<td>$u_i$</td>
<td>pair interaction potential in the spherical shell $i$</td>
</tr>
<tr>
<td>$u_p(r)$</td>
<td>perturbation pair interaction potential</td>
</tr>
<tr>
<td>$U$</td>
<td>internal energy</td>
</tr>
<tr>
<td>$V$</td>
<td>volume</td>
</tr>
<tr>
<td>$x_i$</td>
<td>mole fraction of component $i$</td>
</tr>
<tr>
<td>$Z$</td>
<td>compressibility factor</td>
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</table>

Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>correcting factor</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Boltzmann factor</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>depth of the square-well</td>
</tr>
</tbody>
</table>
\( \xi \) reduced density of mixture
\( \eta \) packing fraction
\( \lambda \) reduced well width of the square-well
\( \rho \) number density of monomers
\( \sigma \) hard-sphere diameter
\( \psi \) correlation coefficient

Subscripts
- 0 reference system
- \( ii \) th component
- \( ij \) a pair of components \( i \) and \( j \)

Acknowledgements

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Appendix A

This appendix contains the residual internal energy (Table 2) and constant-volume heat capacity (Table 3) data obtained by canonical ensemble Monte Carlo simulation for freely-jointed tangent square-well chain mixtures at \( \lambda = 1.5 \).

References