Calculating thermodynamic properties from perturbation theory
II. An analytic representation for the square-well chain fluid

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Abstract
An analytic representation of thermodynamic properties of the freely jointed square-well chain fluid is developed based on the thermodynamic perturbation theory of Barker–Henderson, Zhang and Weitheim. By using a real function expression for the radial distribution function and incorporating structural information for square-well monomer of TPT1 model, an analytic expression for the Helmholtz energy of square-well chain fluid is expanded from Zhang’s analytic expressions for thermodynamic properties of square-well monomer. The expression leads to good predictions of the compressibility factor, residual internal energy and constant-volume heat capacity for 4-mer, 8-mer and 16-mer square-well fluids when compared with the Monte Carlo (MC) simulation results. The incorporating structural information for square-well dimer of TPT-D model is also calculated. To obtain the constant-volume heat capacity needed, \( NVT \) MC simulations were performed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Statistical mechanics; Model; Molecular simulation; Equation of state; Heat capacity

1. Introduction

Perturbation theories have provided a decisive step in understanding and calculating the thermodynamic properties of classical fluids. The thermodynamic properties of chain-like molecule fluids are of interest in theory and for industrial applications. Several theories have been proposed to predict the properties of chain-like fluids [1–6]. The freely jointed hard-sphere chain model has been the subject of recent investigations since it contains the essential features of polymeric molecules, and the development of theory for this model is easier than for more realistic chain-like fluids.

Despite their relative simplicity, the square-well chain fluid models provide a better understanding of the effects of molecular interactions, excluded-volume and segment connectivity on the macroscopic properties of such fluids. In addition, comparing the model results from the experimental data for real systems, enables us to check to which extent a hypothetical system approximates a real system. More
important, these models may provide a useful reference system in statistical mechanical perturbation
theories for chain-like molecular fluids.

There have been some models for equation of state based on the perturbation theory for the square-well
chain fluids [7–12]. However, few of such models are used for the heat capacity. The role of heat capacity
both in applications and in thermodynamics is essential. Two approaches are susceptible for the study of
the model fluids: the theoretical prediction method, as well as the simulation method. Here, we derive a
completely analytic representation of perturbation theory for idealized freely jointed square-well chain fluids,
that the compressibility factors, residual internal energy and constant-volume heat capacity can be
predicted. The primary purpose of this paper is to extend our earlier works [13,14] to chain-like molecule
fluids.

2. Theory

The Helmholtz energy is of interest since it is the quantity from which other thermodynamic prop-
the Helmholtz free energy of chain molecule fluids to the Helmholtz energy of monomer fluids at the
same reduced density and temperature (TPT1). Both Chang and Sandler [12], and Ghonasgi and Chap-
man [14], developed a modified version of Weitheim’s thermodynamic perturbation theory (TPT-D) for
hard-sphere chain fluids. In this section, we derive an analytic representation of the Helmholtz energy for
the square-well chain fluid based on TPT1, TPT-D and Zhang’s [15,16] perturbation theory. The ideal-
ized chain fluid is composed of homonuclear, freely jointed fixed bond length equal to the hard-sphere
diameter \( \sigma \). No angle constraints are imposed on the bonded segments. The Helmholtz energy for the
chain molecules is expressed as

\[
\frac{A_{\text{chain}}^R}{NkT} = \frac{A_{\text{mono}}^R}{NkT} + \frac{A_{\text{pert}}^R}{NkT}
\]

where \( A_{\text{chain}}^R \) and \( A_{\text{mono}}^R \) are the Helmholtz energies of the chain and monomer fluids in excess of that for
the ideal gas state at the same temperature and monomer density, \( N \) the number of chain molecules, and
\( A_{\text{pert}}^R \) the excess Helmholtz energy term due to the bond constraints at the same temperature and monomer
density.

To obtain an analytic expression for the Helmholtz free energy of a chain fluid, one needs analytic
expressions for the radial distribution function and the Helmholtz energy of the square-well monomer
fluid. The analytic perturbation theory including higher-order term derived previously by Zhang [15,16] is
used here to calculate the thermodynamic properties of the square-well monomer. Consider a chain fluid
consisting of \( m \) segments per chain molecule. Every segment is expressed in terms of the perturbation
term for the square-well potential hard-sphere fluid at the same monomer packing fraction \( \eta = \pi \rho \sigma^3/6 \),
the \( A_{\text{mono}}^R \) can be given by

\[
\frac{A_{\text{mono}}^R}{NkT} = m \left( \frac{A^R}{NkT} \right)_{m=1}^m = -12m \alpha \left[ \exp \left( \frac{b \varepsilon}{\alpha} \right) - 1 \right] \sum_{j=1}^{\infty} C_j \left( \frac{\eta}{1-\eta} \right)^j
\]

where \( \varepsilon \) is the well depth, \( b = (kT)^{-1} \), \( \alpha \) the correcting factor defined by Zhang [15] to improve
Barker–Henderson’s \[17,18\] macroscopic compressibility approximation

\[
\alpha = \frac{\beta}{1 + 2K\eta^2} \left( \frac{\partial P}{\partial \rho} \right)_0
\]

(3)

where \( K \) is a proportionality constant for the correlativity of the number of molecules in every two neighbor shells \[17\]. The value of \( K \) can be obtained by \( K \approx 1/\eta_{\text{con}}^2 \) \[15\] with \( \eta_{\text{con}} = 0.493 \) \[19\] when the fluid has condensed. \((\partial P/\partial \rho)_0\) is the compressibility of the reference hard-sphere fluid. When the PY hard-sphere compressibility equation \[20\] is used, we have

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

(4)

and if replace the PY equation with the Carnahan–Starling hard-sphere pressure equation \[21\], we get

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

(5)

Parameter \( C_j \) in Eq. (2) is defined as

\[
C_j = \int_1^{\lambda} \bar{g}_{0j} R^2 dR
\]

(6)

here \( \lambda = 1.5 \) is the width of the square-well and \( R = r/\sigma \) is the reduced distance of interacting particles and \( \bar{g}_{0j} \) \((j = 1, 2, 3, \ldots)\) are the truncated coefficients of the radial distribution function for the reference hard-sphere fluid. This radial distribution function utilized by Zhang \[16\] is

\[
g_0(R) = \frac{1}{\eta} \sum_{j=1}^{\infty} \bar{g}_{0j} \left( \frac{\eta}{1 - \eta} \right)^j
\]

(7)

and the coefficients of the fist four terms are

\[
\begin{aligned}
\bar{g}_{01} &= 1 \\
\bar{g}_{02} &= 7 - 6R + 0.5R^3 \\
\bar{g}_{03} &= 21.019724 - 60.405915R^{-1} + 39.886191R^{-2} \\
\bar{g}_{04} &= -9.100022 + 13.686797R^{-1} - 4.586775R^{-2}
\end{aligned}
\]

(8)

According to the TPT1 theory \[11\], the total contribution of bond formation is calculated by assuming independence with respect to chain size, so that the overall effect of bonding is approximated by the contribution of forming one bond (square-well dimer from square-well monomers) multiplied by the total number of bonds \( N(m - 1) \) in the chain. The Helmholtz energy of this dimerization process at constant temperature and monomer density can be obtained from the integration of the potential of mean force between two randomly chosen molecules from infinite separation to the specified bonding distance \[3,9,12\], and for the square-well potential, the expression of \( A_{\text{pert}}^R \) is

\[
\left( \frac{A_{\text{pert}}^R}{NkT} \right)_{\text{TPT1}} = -(m - 1)[\ln g^{\text{SWS}}(\sigma^+, \eta, \beta \varepsilon) - \ln g^{\text{SWS}}(\sigma^+, \eta \to 0, \beta \varepsilon)]
\]

(9)
The term $g_{\text{SWS}}(\sigma^+, \eta, \beta \varepsilon)$ is the limiting value of the radial distribution function of square-well monomers (SWS) at the segment contact point $\sigma^+$ when approached from larger distance between molecules. The last term in Eq. (9), $\ln g_{\text{SWS}}(\sigma^+, \eta \rightarrow 0, \beta \varepsilon)$, is included to obtain a consistent result in the ideal gas limit. This term is always positive for the square-well potential.

In the TPT-D equation, structural information about the dimer fluid is included to account approximately for the interdependence of bond formation during polymerization. The polymerization process is considered to occur in two steps. First, the SWS react to form square-well dimmers (SWD) and the contribution is evaluated as before. Then the dimer fluid is used as a new reference fluid for higher order polymerization steps. Analogous to the discussion for TPT1, the overall effect of bonding in this second step is approximated by the contribution of one dimerization of the dimer molecules multiplied by the total number of bonds $(m - 2)/2$ that are needed to form a polymer. The perturbation Helmholtz energy is expressed as in the TPT-D model [23]

\[
\left( \frac{A_{\text{pert}}^R}{NkT} \right)_{\text{TPT-D}} = -\frac{m}{2} \left[ \ln g_{\text{SWS}}(\sigma^+, \eta, \beta \varepsilon) - \ln g_{\text{SWS}}(\sigma^+, \eta \rightarrow 0, \beta \varepsilon) \right]
- \left( \frac{m - 2}{2} \right) \left[ \ln g_{\text{SWD}}(\sigma^+, \eta, \beta \varepsilon) - \ln g_{\text{SWD}}(\sigma^+, \eta \rightarrow 0, \beta \varepsilon) \right]
\]

The term $g_{\text{SWD}}(\sigma^+, \eta, \beta \varepsilon)$ is the limiting value of the site–site angle-averaged correlation function of square-well dimers at the segment contact point $\sigma^+$ when approached from infinite site–site separation distance.

The two term $g_{\text{SWS}}$ and $g_{\text{SWD}}$ mentioned above, as function of temperature and monomer density, are important in the derivation of the thermodynamic consistent expressions for the thermodynamic properties. They are expressed similarly to that of Zhang [16]

\[
g_{\text{SWS}}(\sigma^+, \eta, \beta \varepsilon) = g_{\text{SWS}}(\eta) = \frac{1}{\eta} \sum_{i=0}^{4} \sum_{j=1}^{4} a_{ij}(\beta \varepsilon)^i \left( \frac{\eta}{1 - \eta} \right)^j
\]  
\[
g_{\text{SWD}}(\sigma^+, \eta, \beta \varepsilon) = g_{\text{SWD}}(\eta) = \frac{1}{\eta} \sum_{i=0}^{4} \sum_{j=1}^{4} b_{ij}(\beta \varepsilon)^i \left( \frac{\eta}{1 - \eta} \right)^j
\]

and

\[
g_{\text{SWS}}(\sigma^+, \eta \rightarrow 0, \beta \varepsilon) = g_{\text{SWS}}(0) = \sum_{i=0}^{4} a_{ij=1}(\beta \varepsilon)^i
\]  
\[
g_{\text{SWD}}(\sigma^+, \eta \rightarrow 0, \beta \varepsilon) = g_{\text{SWD}}(0) = \sum_{i=0}^{4} b_{ij=1}(\beta \varepsilon)^i
\]

We have used the Monte Carlo (MC) simulation results from the literature to evaluate the parameters $a_{ij}$ and $b_{ij}$ in Eqs. (11) and (12). Eqs. (11) and (12) correlate simulation data with an absolute average deviation (AAD) of 0.1 and 0.2%, respectively, over the temperature–density range $0 \leq \beta \varepsilon \leq 0.7$, $0 \leq \eta \leq 0.5$. The parameters in Eqs. (11) and (12) are listed in Tables 1 and 2, respectively.

Eqs. (2) and (9) are substituted into Eq. (1), lead to an analytic expression for the Helmholtz energy of the square-well chain fluid, and if replace Eq. (9) with Eq. (10), another analytic expression is obtained.
By usual derivations, one obtains the analytical expressions for other thermodynamic properties, which are as follows.

1. The compressibility factor

\[ Z_{\text{chain}}^R = Z_{\text{chain}} - Z_0 = \eta \frac{\partial}{\partial \eta} \left( \frac{A_{\text{mono}}^R}{NkT} + \frac{A_{\text{pert}}^R}{NkT} \right) = Z_{\text{mono}} + Z_{\text{pert}} \quad (15) \]

by substituting Eq. (2) into Eq. (15)

\[ Z_{\text{mono}} = -12m \eta \left\{ \frac{\partial}{\partial \eta} \left[ \frac{1}{\alpha \sum \infty j=1 C_j \left( \frac{\eta}{1-\eta} \right)^j \exp \left( \frac{\beta \varepsilon}{\alpha} \right) - 1 \right] \right\} \]

\[ \frac{\beta \varepsilon}{\alpha} \frac{\partial}{\partial \eta} \left[ \exp \left( \frac{\beta \varepsilon}{\alpha} \right) \sum \infty j=1 C_j \left( \frac{\eta}{1-\eta} \right)^j \right] \quad (16) \]

by substituting Eq. (9) into Eq. (15)

\[ (Z_{\text{pert}})_{\text{TPT1}} = -(m-1) \left[ \frac{\partial \ln g^{\text{SWS}}(\eta)}{\partial \ln \eta} \right] \quad (17) \]

or substituting Eq. (10) into Eq. (15)

\[ (Z_{\text{pert}})_{\text{TPT-D}} = \frac{m}{2(m-1)} (Z_{\text{pert}})_{\text{TPT1}} - \left( \frac{m-2}{2} \right) \left[ \frac{\partial \ln g^{\text{SWD}}(\eta)}{\partial \ln \eta} \right] \quad (18) \]
In Eq. (15), $Z_0$ for reference fluid is expressed as

$$Z_0 = 1 + 4m\eta g_0 (\sigma^+).$$

(19)

2. The residual internal energy

$$\frac{U_{\text{chain}}^R}{NkT} = \beta \frac{\partial}{\partial \beta} \left( \frac{A_{\text{mono}}^R}{NkT} + \frac{A_{\text{pert}}^R}{NkT} \right) = \frac{U_{\text{mono}}^R}{NkT} + \frac{U_{\text{pert}}^R}{NkT}$$

(20)

by substituting Eq. (2) into Eq. (20)

$$\frac{U_{\text{mono}}^R}{NkT} = -12m\beta \varepsilon \exp \left( \frac{\beta \varepsilon}{\alpha} \right) \sum_{j=1}^{\infty} C_j \left( \frac{\eta}{1 - \eta} \right)^j$$

(21)

by substituting Eq. (9) into Eq. (20)

$$\left( \frac{U_{\text{pert}}^R}{NkT} \right)_\text{TPT1} = -m \left\{ \frac{\partial [\ln g^{\text{SW5}}(\eta) - \ln g^{\text{SW5}}(0)]}{\partial \ln \beta} \right\}$$

(22)

or substituting Eq. (10) into Eq. (20)

$$\left( \frac{U_{\text{pert}}^R}{NkT} \right)_\text{TPT-D} = m \left\{ \frac{\partial^2 [\ln g^{\text{SW5}}(\eta) - \ln g^{\text{SW5}}(0)]}{\partial \ln \beta^2} \right\}$$

(23)

3. The constant-volume heat capacity

$$\frac{C_V^\text{chain}}{Nk} = -\beta^2 \frac{\partial^2}{\partial \beta^2} \left( \frac{A_{\text{mono}}^R}{NkT} + \frac{A_{\text{pert}}^R}{NkT} \right) = \frac{C_{V\text{mono}}}{Nk} + \frac{C_{V\text{pert}}}{Nk}$$

(24)

by analogy

$$\frac{C_{V\text{mono}}}{Nk} = 12m \frac{(\beta \varepsilon)^2}{\alpha} \exp \left( \frac{\beta \varepsilon}{\alpha} \right) \sum_{j=1}^{\infty} C_j \left( \frac{\eta}{1 - \eta} \right)^j$$

(25)

$$\left( \frac{C_{V\text{pert}}}{Nk} \right)_\text{TPT1} = (m-1) \left\{ \frac{\partial^2 [\ln g^{\text{SW5}}(\eta) - \ln g^{\text{SW5}}(0)]}{\partial (\ln \beta)^2} \right\}$$

(26)

$$\left( \frac{C_{V\text{pert}}}{Nk} \right)_\text{TPT-D} = \frac{m}{2(m-1)} \left( \frac{C_{V\text{pert}}}{Nk} \right)_\text{TPT1} + \frac{m-2}{2} \left\{ \frac{\partial^2 [\ln g^{\text{SW5}}(\eta) - \ln g^{\text{SW5}}(0)]}{\partial (\ln \beta)^2} \right\}$$

(27)

3. Monte Carlo simulation

In this section, canonical ensemble MC simulations for freely jointed tangent square-well chain fluids (4-mer, 8-mer and 16-mer) are used to obtain the constant-volume capacity. A conventional NVT MC method similar to that of Chang et al. [22] and Tavares et al. [23] is used.
In NVT MC computer simulation, the configuration energy is related to the microscopic structure of the fluid by the energy equation. In the energy equation for chain molecules, the configuration energy of the system, $U_{\text{chain}}$, is the ensemble average of the total potential energy, which consists of intra- and inter-molecular energies,

$$U_{\text{chain}} = \langle U \rangle = \langle U_{\text{inter}} + U_{\text{intra}} \rangle$$

(28)

and

$$U_{\text{inter}} = \sum_{i<j} \sum_{\alpha,\beta} u_{ij}^{\alpha\gamma}(r_{ij}^{\alpha\gamma}), \quad U_{\text{intra}} = \sum_{i} \sum_{\alpha<\beta} u_{ij}^{\alpha\gamma}(r_{ij}^{\alpha\gamma})$$

(29)

where the angular bracket denotes the ensemble average, and $U_{\text{inter}}$ and $U_{\text{intra}}$ are the inter- and intra-molecular energies, respectively. The quantity $u_{ij}^{\alpha\gamma}$ is the site–site potential energy between site $\alpha$ of molecule $i$ and site $\gamma$ of molecule $j$, and is assumed to be a function only of the site–site distance $r_{ij}^{\alpha\gamma}$. For square-well site–site potential energies, it is given by

$$u_{ij}^{\alpha\gamma}(r_{ij}^{\alpha\gamma}) = \begin{cases} \infty, & r_{ij}^{\alpha\gamma} < \sigma \\ -\varepsilon, & \sigma \leq r_{ij}^{\alpha\gamma} < \lambda \sigma \\ 0, & r_{ij}^{\alpha\gamma} \geq \lambda \sigma \end{cases}$$

(30)

where $\sigma$ is the hard core diameter, $\varepsilon$ is the well depth, and $\lambda$ is the well width of the site–site potential. Throughout this work, we have used $\lambda = 1.5$.

The constant-volume heat capacity is obtained by

$$\frac{C_V}{Nk} = N \left[ \left\langle \left( \frac{U}{NkT} \right)^2 \right\rangle - \left\langle \frac{U}{NkT} \right\rangle^2 \right]$$

(31)

In the simulations, we studied square-well chains composed of $m$ freely jointed, no overlapping tangent spheres (in three-dimensions) of unit diameter. The simulation cell was a cube with periodic boundary conditions and the minimum image convention. We used 256 molecules for each chain fluid. The Metropolis criterion is used to decide whether an attempted configuration is accepted or not. Within a cycle an attempt is made to translate the first segment of each chain molecule and to reorient the bond vector, which satisfies the microscopic reversibility. The maximum size for each type of move is adjusted to give a 50% acceptance ratio. The initial configurations were prepared by inserting the chain segments randomly into a cubic box for low reduced densities, while at high densities compression of the box of a previous simulation was accomplished using the usual MC simulation until the desired density was obtained. With a given initial configuration, the system was first relaxed to equilibrium, requiring more than $5 \times 10^5$ cycles. During each cycle, translations and rotations of all molecules were attempted. After equilibration, the thermodynamic properties were calculated using another $5 \times 10^5$ cycles. Results are listed in Table 3 in Appendix A.

4. Result and discussion

In this section, comparisons are made between the thermodynamic properties predicted from the proposed analytic representations and the results from MC simulations for the freely jointed square-well chain
Fig. 1. Values of $g^{SWS}(\sigma^+, \eta, \beta \varepsilon)$ for the square-well fluid with $\lambda = 1.5$ at four different reduced temperature $\beta \varepsilon = 0.667, 0.5, 0.333$ and 0.25. The open symbols are the MC results of Tavares et al. [23] and Henderson et al. [24]. The curves are obtained from Eq. (11).

fluid with well width $\lambda = 1.5$. We will be primarily concerned with its performance for the predictions of the compressibility factor, residual internal energy and constant-volume heat capacity.

The radial distribution function for the square-well monomer $g^{SWS}(\sigma^+, \eta, \beta \varepsilon)$ at contact point $\sigma^+$ along various isotherms $\beta \varepsilon$ is calculated by Eq. (11) and shown in Fig. 1 as a function of reduced density $\eta$.

Fig. 2. Values of $g^{SWD}(\sigma^+, \eta, \beta \varepsilon)$ for the square-well fluid with $\lambda = 1.5$ at five different reduced temperature $\beta \varepsilon = 0.667, 0.5, 0.333, 0.25$ and 0. The open symbols are the MC results by Tavares et al. [23] and Chang and Sandler [22]. The curves are obtained from Eq. (12).
Fig. 3. The compressibility factor of square-well dimer, 4-mer, 8-mer and 16-mer chains with \( \lambda = 1.5 \) at reduced temperature \( \beta \varepsilon = 0.5, 0.333 \) and 0.25. The lines are results of this work (‘a’ denotes the approach of TPT1 and ‘b’ denotes that of TPT-D). The open symbols are MC results of Tavares et al. [23].

MC results by Tavares et al. [23] and Henderson et al. [24] are plotted for comparison. The site–site correlation function \( g^{\text{SWD}}(\sigma^+, \eta, \beta \varepsilon) \) is calculated by Eq. (12) and shown in Fig. 2. MC results by Tavares et al. [23] and Chang and Sandler [12] are shown, too. From Figs. 1 and 2, we can conclude that Eqs. (11) and (12) are successful expressions for \( g^{\text{SWS}} \) and \( g^{\text{SWD}} \) at contact bond length \( \sigma^+ \).

In Fig. 3, the compressibility factors of the dimer, 4-mer, 8-mer and 16-mer square-well chain fluids predicted from the proposed representations Eqs. (15)–(19) are compared with the MC simulation results cited by Tavares et al. [23].

In Fig. 4, we compare the predictions of the residual internal energies from Eqs. (20)–(23) with the MC simulation results by Tavares et al. [9] for the 4-mer, 8-mer and 16-mer square-well chain fluids.

In Fig. 5, the constant-volume heat capacity predicted from Eqs. (24)–(27) are compared with the MC simulation results for the 4-mer, 8-mer and 16-mer square-well chain fluids at reduced density \( \eta = 0.262 \).

In these figures, the predictions based on Eq. (9) (TPT1) are denoted by ‘a’ and based on Eq. (10) (TPT-D) by ‘b’. From these figures, we can see that the analytic expressions based on Eq. (9), for compressibility factor, residual internal energy and constant-volume heat capacity for square-well chain fluids, are in good agreement with the simulation data. Johnson [25] has improved the low density internal energy behavior of L–J chain fluid by using a higher order reference fluid. But no improvement is made
Fig. 4. The reduced residual internal energy of square-well 4-mer, 8-mer and 16-mer chains with $\lambda = 1.5$ at reduced temperature $\beta\varepsilon = 0.5, 0.333$ and 0.25. The lines are results of this work (‘a’ denotes the approach of TPT1 and ‘b’ denotes that of TPT-D). The open symbols are MC results by Tavares et al. [5].

Fig. 5. The reduced constant-volume heat capacity of square-well 4-mer with $\lambda = 1.5$ at reduced density $\eta = 0.5\pi/6$. The lines are results of this work (‘a’ denotes the approach of TPT1 and ‘b’ denotes that of TPT-D). The open symbols are the MC simulation results of this work.

when we attempted to improve the accuracy of prediction at low density by the approach which is expressed as Eq. (10) (TPT-D model). This may be due to the limitation of the potential model.

5. Conclusion

In this work, Zhang’s analytic representations of the thermodynamic properties for a square-well monomer are expanded to the freely jointed square-well chain fluid. The expressions do not contain adjustable parameters, and lead to good predictions of the compressibility factor, residual internal energy and the constant-volume heat capacity for dimer, 4-mer, 8-mer and 16-mer square-well chain fluids when compared with MC data. The Helmholtz energy due to bond formation at the same temperature and monomer density is estimated by the first-order perturbation theory of Weitheim (TPT1). To improve
the accuracy of the predictions at low density, the bond formation correlating free energy term is also estimated by TPT-D model, but no superior results are obtained.

List of symbols

- $A$: Helmholtz free energy
- $C_i$: coefficient in Eq. (2)
- $C_V$: constant-volume heat capacity
- $g_0(r)$: radial distribution function of the reference system
- $g_{ij}(r_{ij})$: site–site distribution function
- $\bar{g}_0j$: coefficient of Eq. (7) for $g_0(r)$
- $k$: Boltzmann constant
- $K$: proportion coefficient in Eq. (3)
- $m$: chain length, number of segments per chain molecules
- $N$: total number of chain molecules
- $P$: pressure
- $r$: distance of the interacting particles
- $R$: reduced distance of the interacting particles
- $T$: absolute temperature (K)
- $T^*$: reduced temperature, defined as $T^* = kT/\varepsilon$
- $u_{ij}^{\alpha\gamma}$: site–site potential energy between site $\alpha$ of molecule $i$ and site $\gamma$ of molecule $j$
- $U$: total potential energy
- $V$: volume
- $Z$: compressibility factor $Z = PV/(NkT)$

Greek symbols

- $\alpha$: correcting factor defined as $\alpha = \beta(\partial P/\partial \rho)_0/(1 + 2K\eta^2)$
- $\beta$: Boltzmann factor defined as $\beta = 1/(kT)$
- $\varepsilon$: depth of the square-well
- $\eta$: packing fraction, defined as $\eta = \pi \rho \sigma^3/6$
- $\lambda$: reduced well width of the square-well
- $\rho$: number density
- $\sigma$: hard-sphere diameter

Subscripts and superscripts

- $0$: denotes reference system
- $R$: denotes excess part
- SWS: denotes square-well monomer
- SWD: denotes square-well dimers

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Table 3
Monte Carlo simulation results of constant-volume heat capacity $C_V/(Nk)$ for the 4-mer, 8-mer and 16-mer square-well chains at $\eta = 0.5\pi/6$

<table>
<thead>
<tr>
<th>m</th>
<th>$\beta\varepsilon$</th>
<th>0.5</th>
<th>0.333</th>
<th>0.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.253 ± 0.334</td>
<td>0.502 ± 0.051</td>
<td>0.090 ± 0.023</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2.448 ± 0.625</td>
<td>0.997 ± 0.063</td>
<td>0.262 ± 0.034</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>4.823 ± 0.872</td>
<td>1.718 ± 0.126</td>
<td>0.781 ± 0.065</td>
<td></td>
</tr>
</tbody>
</table>

Appendix A

This appendix contains the constant-volume heat capacity data (Table 3) obtained by canonical ensemble Monte Carlo simulation of freely-jointed tangent square-well dimer, 4-mer, 8-mer and 16-mer chain fluid at $\lambda = 1.5$.

References