

MOLECULAR DYNAMIC SIMULATION AND EQUATION OF STATE OF LENNARD-JONES CHAIN FLUIDS

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Abstract – In order to study the thermodynamic properties of chain and polymeric fluids at the molecular level, we perform constant temperature molecular dynamics simulations of 'repulsive' and 'full' Lennard-Jones (LJ) chain fluids of lengths up to 16. In the simulation, the RATTLE algorithm to determine constraint forces and the Nose-Hoover thermostat to sample the canonical ensemble are used. For repulsive LJ chains, the compressibility factor of the chain fluids is predicted from first-order thermodynamic perturbation theory combined with the Week-Chandler-Anderson (TPT1-WCA) perturbation theory, and is compared to the simulation results. A good agreement between the theory and the simulation results is found particularly at liquid-like densities. For full LJ chains, two different versions of TPT1 are used to calculate the compressibility factor: one is TPT1-WCA, and the other is TPT1 with the Percus-Yevick approximation for the radial distribution function of the LJ spheres (TPT1-PY). At low and intermediate densities, TPT1-PY gives better predictions for the compressibility of the LJ chain fluids, whereas at high densities TPT1-WCA is more reliable.

Key words : Equation of State, Molecular Dynamics, Thermodynamic Perturbation Theory, Lennard-Jones, Chain Fluid

INTRODUCTION

An accurate estimation of thermodynamic properties of gases and liquids is important to process design in the chemical and petroleum industries. During the last decade, there has been a considerable interest in developing molecularly based equations of state for chain molecules and polymers. These include generalized Flory-Dimer (GF-D) theory [Honnell and Hall, 1989] and thermodynamic perturbation theory (TPT) [Wertheim, 1987], which is also referred to as statistical associating fluid theory (SAFT) by some researchers [Chapman et al., 1988, 1990; Huang and Radosz, 1990]. The essential feature of the TPT theory is that the Helmholtz energy of chain fluids can be approximated in first order (TPT1) by the Helmholtz energy and the pair correlation function of the reference fluid which is composed of nonbonded monomers. An advantage of the TPT theory in developing equations of state of complex fluids is that one could avoid solving integral equations in order to obtain the thermodynamic properties. Further improvement of TPT for hard-sphere chain fluids includes the second order TPT (TPT2), in which a triplet correlation function of the reference fluid is required [Wertheim, 1987] and the TPT dimer (TPT-D) theory in which a segment-segment correlation function of the dimer reference fluid is used [Chang and Sandler, 1994; Ghonasgi and Chapman, 1994]. Extension of the TPT theory to more realistic chain models has been recently studied including the TPT-D theory for square-well chains [Tavares et al., 1995], the TPT1 theory for the Lennard-Jones (LJ) chains [Johnson et al., 1994; Banaszak et al., 1994].

In the present work we provide molecular dynamics simu-

lation results for freely jointed LJ chains, and test accuracy of equations of state obtained from the TPT1 theory. Two types of LJ potentials interacting between intermolecular and nonbonded intramolecular segments are considered: a potential with only a repulsive part and a 'full' LJ potential. In order to get the thermodynamic and structural properties of the reference fluid (LJ spheres), we use the Week-Chandler-Anderson (WCA) perturbation theory [Weeks et al., 1971] and the Ornstein-Zernike equation with the Percus-Yevick approximation [Lee, 1988]. The equation of state or the compressibility factor of LJ chain fluids is then calculated through the TPT1 theory. Theoretical predictions are compared to computer simulation results, and the validity and accuracy of approximations in the theory are examined.

THEORY

We consider two chain models, 'full' and 'repulsive' LJ chains. In the 'full' LJ chains the intermolecular and nonbonded intramolecular segments interact with each other by the LJ potential

$$u_{ref}^{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

where σ and ϵ are size and energy parameters of the LJ potential, respectively. In the 'repulsive' LJ chains segments interact with each other by 'repulsive' LJ potential given as

$$u_{ref}^{RLJ}(r) = \begin{cases} u_{ref}^{LJ}(r) + \epsilon, & r < 2^{1/6} \sigma \\ 0, & r > 2^{1/6} \sigma \end{cases} \quad (2)$$

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This potential was used as a reference system in the WCA perturbation theory [Weeks et al., 1971] for LJ spheres. In the present work we consider the case that chains are constructed such that bond distance is fixed and equal to the size parameter, $l=\sigma$, and that there is no restriction on bond angles.

The TPT theory was originally developed to treat associating fluids in which intermolecular potentials consist of spherically symmetric potentials and asymmetric associating attractions of short range [Wertheim, 1984a, b, 1986a, b]. It was shown that the theory can be further applied to chain molecules with covalent bonds [Wertheim, 1987]. For associating spheres with two random association sites A and B, the pair potential $u(12)$ has the following form

$$u(12) = u_{ref}(r) + u_{AB}(12) + u_{BA}(12) \quad (3)$$

where $u_{ref}(r)$ is the pair potential of a nonbonded reference system at distance r , and $u_{AB}(12)$ is associating potential between two sites A and B on different spheres (monomers). With this potential, freely jointed linear chains of various lengths are formed at equilibrium, and average chain length, m , depends on the strength of association and thermodynamic variables such as temperature and density. The TPT theory gives the Helmholtz energy of the chain fluid in first order (TPT1) [Wertheim, 1987; Chapman et al., 1988] by

$$A_c' = A_{ref}' - N(m-1)k_B T \ln y_{ref}(l) \quad (4)$$

where A_c' and A_{ref}' are the residual or excess Helmholtz energies of the chain and monomer reference fluid, respectively, with respect to those of the ideal gases at the same temperature and density, N is the number of chain molecules, k_B is the Boltzmann constant, and $y_{ref}(l)$ is the pair cavity correlation function of the reference fluid at bond distance l . Notice that for the LJ spheres the value of the cavity correlation function at $r=\sigma$ is simply equal to that of radial distribution function (RDF), i.e., $y_{ref}(\sigma) = g_{ref}(\sigma)$. The last term of Eq. (4) represents free energy change of polymerization at fixed temperature and volume, and it can be simply interpreted as the total number of bonds in N chains times the free energy of forming a single bond in the nonbonded reference fluid [Chang and Sandler, 1994].

When chain molecules of fixed length m are involved, as is the case here, Eq. (4) is still applicable since the TPT1 theory is insensitive to polydispersity of chains. Notice that the TPT1 theory cannot account for either intramolecular contribution for flexible chains or bond angle restrictions for freely rotating chains. For the theory to be improved beyond the first order, more information is necessary such as the higher order correlation functions of the reference system or the pair correlation of an additional reference system, for example, dimer fluid. However, little is known about those properties except for hard sphere fluids, and thus our interest is confined to the TPT1 theory for the LJ chains. Other thermodynamic properties can be obtained through thermodynamic relations. The compressibility factor of chain fluid Z_c is given by

$$Z_c = mZ_{ref} - (m-1) \left[1 + \rho \frac{\partial \ln y_{ref}(l)}{\partial \rho} \right] \quad (5)$$

where $Z_c = p/\rho_c k_B T$, p is the pressure, ρ_c is the number density of chains, Z_{ref} is the compressibility of the reference system, and ρ is the number density of monomers.

SIMULATION

Molecular dynamics simulations are performed for repulsive and full LJ freely jointed chains in order to calculate the thermodynamics properties [Allen and Tildesley, 1987]. Unlike simple fluids, chain molecules have many internal degrees of freedom associated with fast vibrational and moderate rotational motions. In simulations the high frequency vibrational motions are often frozen at their equilibrium bond distances because they have little effect on the thermodynamic properties, and the removal of the high frequency vibrational motions render the simulation faster at least about by a factor of two.

In order to predict the time evolution of chains with fixed bond distance, we use method of constraint dynamics in cartesian coordinates. Ryckert et al. [1977] developed the SHAKE algorithm to deal with bond constraints, in which Lagrangian forces due to geometric constraints are iteratively calculated. Later, Andersen [1983] modified the SHAKE algorithm based on the velocity version of Verlet's algorithm, which is called the RATTLE algorithm. The RATTLE algorithm has advantages over the SHAKE algorithm in that both position and velocity are explicitly calculated in the RATTLE algorithm, and by this reason the constant temperature molecular dynamics could be more easily implemented with the RATTLE algorithm. In this study, we used the RATTLE algorithm combined with Nose-Hoover's constant temperature molecular dynamics [Nose, 1984; Hoover, 1985]. The equation of motion of each segment is given by

$$m_{i\alpha} \ddot{\mathbf{r}}_{i\alpha} = \mathbf{f}_{i\alpha} + \sum_{\beta} \lambda_{\alpha\beta} (\mathbf{r}_{i\alpha} - \mathbf{r}_{i\beta}) - m_{i\alpha} \xi \dot{\mathbf{r}}_{i\alpha} \quad (6)$$

where $m_{i\alpha}$ is the mass of segment α of chain i , $\mathbf{r}_{i\alpha}$ is the position vector, the dot denotes differentiation with respect to time, $\mathbf{f}_{i\alpha}$ is force exerted on the segment by other segments except for segments directly bonded to, and ξ is the friction coefficient. The second term of Eq. (6) is the Lagrangian force due to constraint between segment α and segment β . The last term derives the temperature of the system to a desired value. The friction coefficient ξ is given by the first order differential equation

$$\dot{\xi} = \frac{N(2m+1)-3}{Q} k_B (T_{inst} - T_d) \quad (7)$$

where T_{inst} is instantaneous kinetic temperature, T_d is desired temperature, Q is the thermal inertia parameter which controls heat flow between system and imaginary reservoir. The quantity Q can be regarded as a free parameter of the simulation.

Thermodynamic properties such as temperature, configurational energy, and pressure can be calculated from time averages of corresponding microscopic quantities. The temperature of the system is obtained from the sum of the kinetic energy of all segments, referred to as 'atomic temperature',

and is given by

$$T = \frac{2}{k_B [N(2m+1) - 3]} \langle K \rangle \quad (8)$$

where the angular bracket denotes time average and K is the kinetic energy of the system expressed as

$$K = \frac{1}{2} \sum_i^N \sum_\alpha^m m_{i\alpha} \dot{r}_{i\alpha}^2 \quad (9)$$

The pressure is obtained by taking the average of the 'atomic virial', given by

$$p = \frac{1}{3V} \left\langle 2K + \sum_i^N \sum_\alpha^m \mathbf{r}_{i\alpha} \cdot \mathbf{F}_{i\alpha} \right\rangle \quad (10)$$

where V is the the volume and $\mathbf{F}_{i\alpha}$ is force exerted on the segment α of molecule i including all constraint forces. The configurational energy is evaluated by summing up all inter- and nonbonded intramolecular interaction potentials. For the LJ potential, the potential is cut-off at 2.5σ , and long range corrections are considered for intermolecular contributions to the pressure and configuration energy.

RESULTS AND DISCUSSION

Molecular dynamics simulation results for the repulsive LJ chains of lengths 4, 8, and 16 are summarized in Table 1, where the reducible variables are defined as $\rho^* = m\rho\sigma^3$, $T^* = k_B T/\epsilon$, and $U^* = U/mN\epsilon$. During each simulation, the first 2,000 time steps were used to equilibrate the system, and the time average was taken for the next 7,000 time steps. The time integration step was chosen to be 0.004 in reduced unit, with which the Hamiltonian of the closed system remains unchanged during the period of the simulation. Temperatures studied are 1.25 and 3.0, and densities are as high as 0.9 in reduced units. The kinetic temperature of the system is well driven to the desired value within an error of 0.001.

Calculating the compressibility factor from the TPT1 theory requires the Helmholtz energy and the RDF of the reference system. The residual Helmholtz energy of the repulsive LJ spheres is approximated in a similar manner as for the hard spheres, i.e.,

$$\frac{A_{ref}^r}{Nk_B T} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2} \quad (11)$$

Here, the effective packing fraction η is determined from procedure devised by Verlet and Weis [1972]. The RDF of the repulsive LJ spheres is obtained from the approximation suggested by Weeks et al. [1971] which is given by

$$g_{ref}(r) = \exp[-u_{ref}^{LJ}(r)/k_B T] y_{HS}(r) \quad (12)$$

where $y_{HS}(r)$ is the cavity correlation function of the hard spheres. The $y_{HS}(r)$ is obtained from the Percus-Yevick solution with the empirical correction of Verlet and Weis [1972]. From substitution of Eqs. (11) and (12) into Eq. (4) and from the numerical differentiation of the Helmholtz energy with respect to density, we get the compressibility factor of the repulsive LJ chains.

Table 1. MD simulation results for repulsive LJ chains

m	ρ^*	T^*	Z_c	U^*
4	0.1	1.25	1.46	0.027
4	0.2	1.25	2.23	0.045
4	0.3	1.25	3.26	0.071
4	0.4	1.25	4.97	0.11
4	0.5	1.25	7.28	0.17
4	0.6	1.25	10.6	0.27
4	0.7	1.25	15.5	0.41
4	0.8	1.25	22.3	0.61
4	0.9	1.25	32.3	0.93
4	0.1	3.0	1.51	0.073
4	0.2	3.0	2.15	0.12
4	0.3	3.0	3.05	0.18
4	0.4	3.0	4.40	0.28
4	0.5	3.0	6.23	0.42
4	0.6	3.0	8.84	0.63
4	0.7	3.0	12.3	0.92
4	0.8	3.0	17.2	1.34
4	0.9	3.0	23.7	1.93
8	0.1	1.25	1.76	0.029
8	0.2	1.25	2.99	0.045
8	0.3	1.25	5.01	0.065
8	0.4	1.25	7.95	0.10
8	0.5	1.25	12.3	0.15
8	0.6	1.25	18.8	0.24
8	0.7	1.25	28.1	0.36
8	0.8	1.25	41.3	0.55
8	0.9	1.25	61.4	0.86
8	0.1	3.0	1.72	0.081
8	0.2	3.0	2.93	0.12
8	0.3	3.0	4.46	0.17
8	0.4	3.0	6.99	0.25
8	0.5	3.0	10.6	0.38
8	0.6	3.0	15.5	0.56
8	0.7	3.0	22.4	0.83
8	0.8	3.0	32.0	1.22
8	0.9	3.0	45.0	1.78
16	0.1	1.25	2.44	0.032
16	0.2	1.25	4.44	0.042
16	0.3	1.25	8.28	0.063
16	0.4	1.25	13.9	0.095
16	0.5	1.25	22.2	0.14
16	0.6	1.25	35.0	0.22
16	0.7	1.25	53.5	0.34
16	0.8	1.25	79.3	0.52
16	0.9	1.25	119.	0.81
16	0.1	3.0	2.25	0.085
16	0.2	3.0	4.27	0.12
16	0.3	3.0	7.49	0.17
16	0.4	3.0	12.0	0.24
16	0.5	3.0	18.9	0.35
16	0.6	3.0	28.8	0.53
16	0.7	3.0	42.5	0.78
16	0.8	3.0	61.0	1.15
16	0.9	3.0	87.5	1.70

In Figs. 1-3, we show the predictions of the theory and computer simulation results for the compressibility factor of

the repulsive LJ chains of $m=4$, 8, and 16. It is seen that the TPT1 theory gives accurate predictions for the repulsive chains particularly at high densities, and that the theory is able to account for the temperature dependence of the compressibility factor satisfactorily. The higher the temperature, the lower the compressibility factor. This is because the effective hard sphere diameter of the LJ spheres decreases with increasing temperature. Although the TPT theory gives the correct ideal gas limit, it slightly overestimates the compressibility factor at low and intermediate densities. This is due to the fact that the effect of intramolecular interactions is neglected in the first order theory. The theory, however, gives very accurate predictions at high densities where the intermolecular contributions are dominant. Also shown in Fig. 3 are the results of the molecular dynamics simulation of Gao and Weiner [1989] at $T^*=1.25$ and of force-biased Monte Carlo

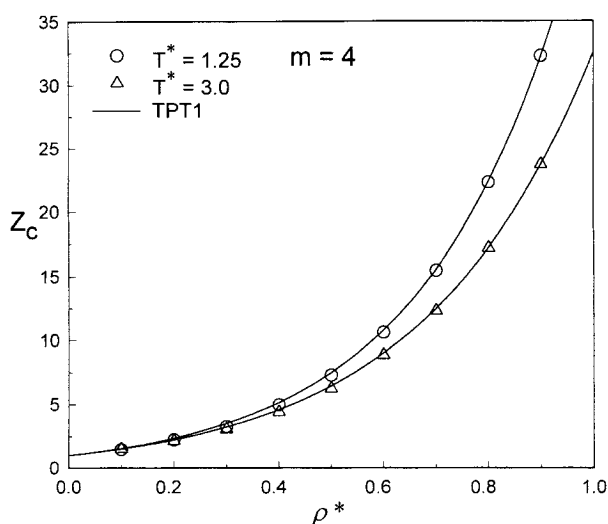


Fig. 1. The compressibility factor of the repulsive LJ chains of length $m=4$. Symbols are MD simulation results, and lines are from the TPT1 theory.

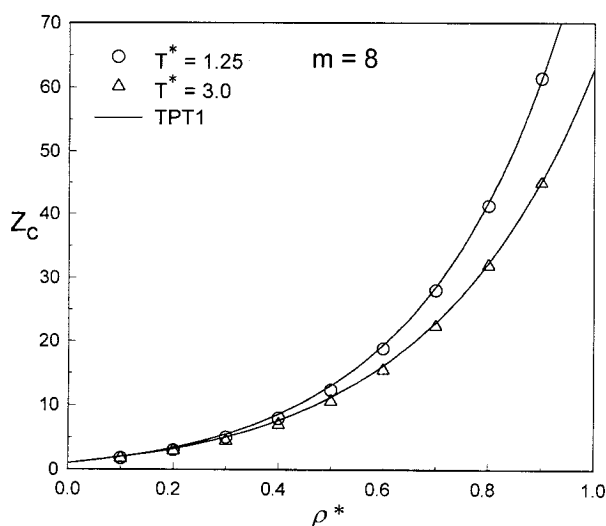


Fig. 2. The compressibility factor of the repulsive LJ chains of length $m=8$. Lines and symbols have the same meaning as in Fig. 1.

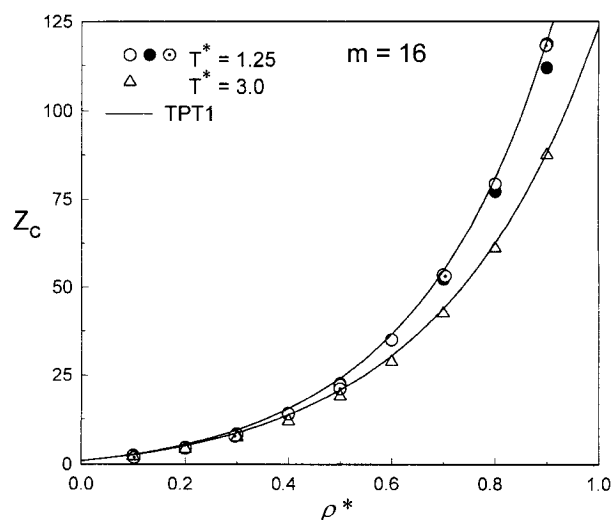


Fig. 3. The compressibility factor of the repulsive LJ chains of length $m=16$. Open symbols are the MD simulation results of the present work, solid symbols are the MD simulation results of Gao and Weiner [1989], and dotted symbols are the MC simulation results of Li and Chiew [1994a]. Lines are from the TPT1 theory.

simulation of Li and Chiew [1994a]. In Gao and Weiner's simulation harmonic bond vibrations are allowed. They used an arbitrarily large value for the spring constant to mimic infinitely stiff chains. A consistent agreement is found between these simulation results.

For the full LJ chains two different methods of calculating the compressibility factor are used. In the first method, the bond contribution term in Eq. (5) is calculated in the same manner as for the repulsive LJ chains, i.e., by using Eq. (12), which is referred to as TPT1-WCA. This is essentially the same method as Banaszak et al. [1994] used with the difference that we do not utilize an empirical fitting. Since it is known in the WCA perturbation theory that the RDF obtained from Eq. (12) is reasonable at high temperatures and at liquid-like densities, a good accuracy is thus expected at such conditions for chain fluids. In the second method, referred to as TPT1-PY, the RDF of the full LJ spheres is calculated by solving the Ornstein-Zernike equation with the Percus-Yevick (PY) closure approximation. The details of solving the integral equation can be found elsewhere [Lee, 1988], and we plot in Fig. 4 the solution for the RDF at the bond distance σ at temperatures $T^*=2.0$, 3.0 and 5.0. Also shown is an empirically fitted curve for this temperature and density range given as

$$g_{reg}(\sigma) = 1 + 0.648\rho^* + 1.025\rho^{*2} - 0.513\rho^{*3} - T^{*-1}(0.923\rho^* + 1.228\rho^{*2} - 3.317\rho^{*3}) \quad (13)$$

TPT1-WCA and TPT1-PY differ from each other in the ways of obtaining the RDF of the monomer reference fluid. To get the compressibility factor of the LJ spheres, we used Nicolas et al.'s [1979] equation of state, which is an empirical equation of state with parameters determined from fitting computer simulation data.

The simulation results for chains of $m=4$, 8, and 16 are list-

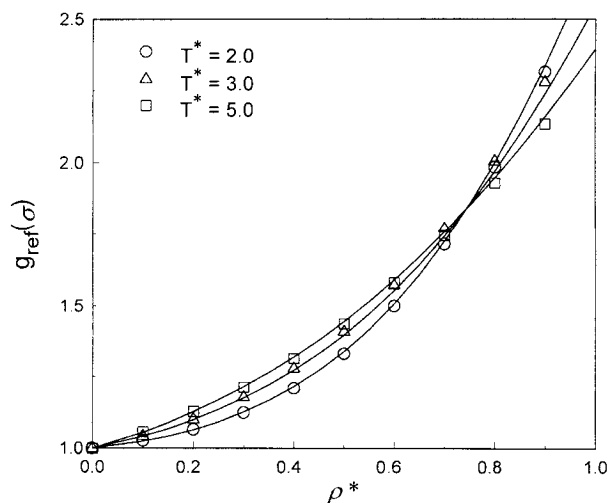


Fig. 4. The values of the radial distribution function of LJ spheres at the bond distance σ . Symbols are calculated from the Ornstein-Zernike equation with the PY approximation, and lines are from the fitted polynomial, Eq. (13).

ed in Table 2, and are compared to the predictions of the theories in Fig. 5, 6, and 7, respectively. Also shown for comparison are the results of molecular dynamics simulation results of Johnson et al. [1994] and of Monte Carlo simulation of Li and Chiew [1994b]. The simulation results from different sources including those of the present work agree well with one another, while the details of the chain models and the simulation schemes are slightly different. The bond vibrations are frozen in Johnson et al.'s simulation by using an arbitrarily large spring constant, while in the present work the chains with rigid bonds are employed.

As expected, TPT-WCA well predicts the compressibility factor at high temperatures and at liquid-like densities. However, its accuracy worsens as temperature or density decreases. TPT1-PY gives more accurate predictions than TPT1-WCA particularly at low and moderate densities. This is clearly because the RDF of the LJ fluids obtained from the integral equation is more reliable than that from the perturbation theory at low and intermediate densities. At the lowest temperature studied in the present work, $T^*=2.0$, the 8- and 16-mer fluids clearly have vapor-liquid transitions as can be seen from Figs. 6 and 7, and the single phase simulation of this work gives negative values for the compressibility factor, which implies instability of the system.

Next, we predict vapor-liquid equilibria (VLE) of the LJ chain fluids from the TPT1-PY equation of state, and show the coexisting curve and vapor pressure in Figs. 8 and 9, respectively. The predicted VLE shows the essential features of chain fluids with increasing molecular sizes. In Fig. 8, the critical temperature increases with the increasing chain length, the critical density shifts toward the gas phase, and the phase envelope becomes asymmetric as the chain length increases. In Fig. 9, as the chain length increases, the vapor pressure decreases and its slope (the heat of vaporization) increases. While a more quantitative comparison awaits Gibbs ensemble

Table 2. MD simulation results for full LJ chains

m	ρ^*	T^*	Z_c	U^*
4	0.1	2.0	0.50	-0.86
4	0.2	2.0	0.15	-1.35
4	0.3	2.0	-0.20	-1.83
4	0.4	2.0	-0.31	-2.28
4	0.5	2.0	-0.21	-2.76
4	0.6	2.0	0.36	-3.33
4	0.7	2.0	2.25	-3.91
4	0.8	2.0	5.83	-4.47
4	0.9	2.0	12.3	-4.90
4	0.1	3.0	0.84	-0.67
4	0.2	3.0	0.76	-1.11
4	0.3	3.0	0.81	-1.57
4	0.4	3.0	0.93	-2.05
4	0.5	3.0	1.53	-2.56
4	0.6	3.0	2.70	-3.09
4	0.7	3.0	4.79	-3.60
4	0.8	3.0	8.30	-4.04
4	0.9	3.0	13.7	-4.31
4	0.1	5.0	1.06	-0.56
4	0.2	5.0	1.22	-0.93
4	0.3	5.0	1.54	-1.36
4	0.4	5.0	2.05	-1.80
4	0.5	5.0	2.84	-2.25
4	0.6	5.0	4.17	-2.69
4	0.7	5.0	6.38	-3.04
4	0.8	5.0	9.52	-3.27
4	0.9	5.0	14.0	-3.28
8	0.1	2.0	-0.08	-1.18
8	0.2	2.0	-0.62	-1.62
8	0.3	2.0	-1.22	-1.94
8	0.4	2.0	-1.64	-2.31
8	0.5	2.0	-1.98	-2.74
8	0.6	2.0	-1.11	-3.26
8	0.7	2.0	2.13	-3.85
8	0.8	2.0	8.97	-4.41
8	0.9	2.0	21.5	-4.87
8	0.1	3.0	0.69	-0.80
8	0.2	3.0	0.41	-1.20
8	0.3	3.0	0.39	-1.63
8	0.4	3.0	0.59	-2.04
8	0.5	3.0	1.47	-2.52
8	0.6	3.0	3.47	-3.04
8	0.7	3.0	7.21	-3.56
8	0.8	3.0	14.3	-4.01
8	0.9	3.0	25.0	-4.32
8	0.1	5.0	1.07	-0.66
8	0.2	5.0	1.25	-0.99
8	0.3	5.0	1.68	-1.37
8	0.4	5.0	2.58	-1.81
8	0.5	5.0	4.06	-2.24
8	0.6	5.0	6.58	-2.67
8	0.7	5.0	10.6	-3.06
8	0.8	5.0	16.8	-3.31
8	0.9	5.0	25.4	-3.39

Table 2. Continued

m	ρ^*	T^*	Z_c	U^*
16	0.1	2.0	-0.52	-1.42
16	0.2	2.0	-2.01	-1.81
16	0.3	2.0	-3.09	-2.06
16	0.4	2.0	-4.46	-2.37
16	0.5	2.0	-4.82	-2.76
16	0.6	2.0	-3.85	-3.24
16	0.7	2.0	2.50	-3.81
16	0.8	2.0	15.5	-4.38
16	0.9	2.0	39.8	-4.85
16	0.1	3.0	0.22	-0.98
16	0.2	3.0	0.32	-1.28
16	0.3	3.0	-0.32	-1.64
16	0.4	3.0	-0.18	-2.03
16	0.5	3.0	1.62	-2.52
16	0.6	3.0	5.25	-3.01
16	0.7	3.0	12.3	-3.54
16	0.8	3.0	24.8	-4.01
16	0.85	3.0	35.2	-4.19
16	0.9	3.0	47.2	-4.33
16	0.1	5.0	1.01	-0.74
16	0.2	5.0	1.39	-1.04
16	0.3	5.0	2.19	-1.39
16	0.4	5.0	3.46	-1.78
16	0.5	5.0	6.61	-2.22
16	0.6	5.0	11.3	-2.66
16	0.7	5.0	19.2	-3.06
16	0.75	5.0	24.6	-3.22
16	0.8	5.0	29.8	-3.36
16	0.9	5.0	49.2	-3.41

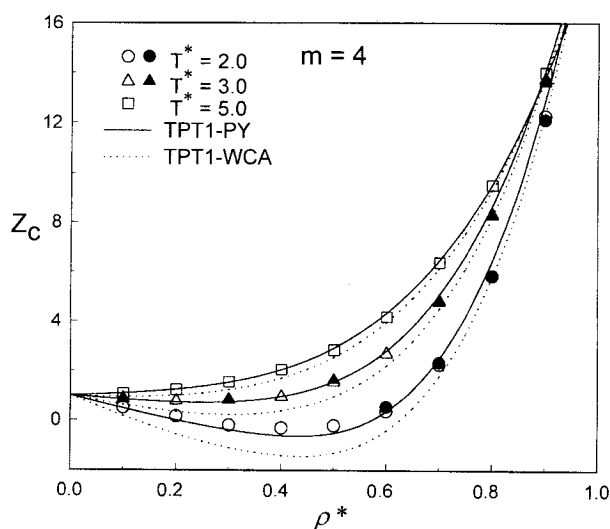


Fig. 5. The compressibility factor of the LJ chains of length $m=4$. Open symbols are the MD simulation results of the present work, solid symbols are the MD simulation results of Johnson et al. [1994], solid lines are from TPT1-PY, and dotted lines are from TPT1-WCA.

simulation data [Panagiotopoulos, 1987], the present work provides an insight into the construction of the equation of state of chain and polymers from knowledge for a fluid of spher-

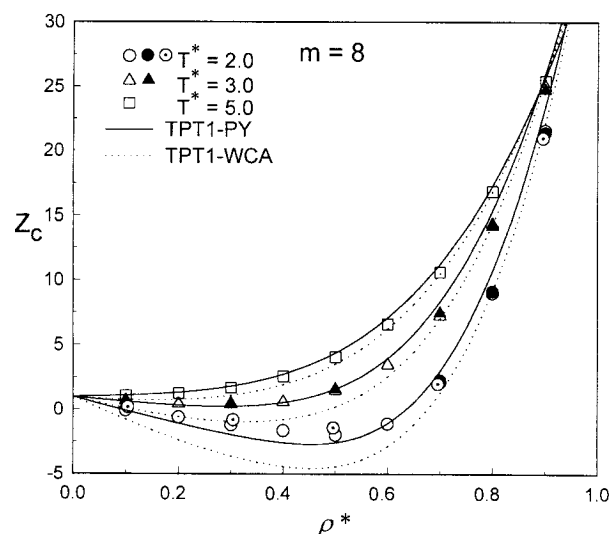


Fig. 6. The compressibility factor of the LJ chains of length $m=8$. Lines and symbols have the same meaning as in Fig. 5. In addition, dotted symbols are the MC simulation results of Li and Chiew [1994b].

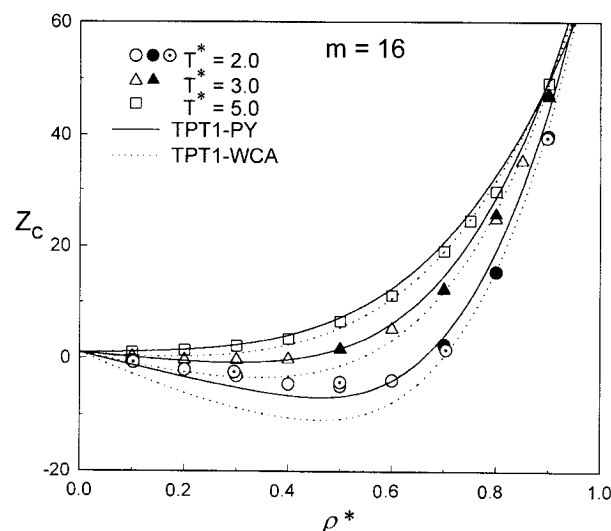


Fig. 7. The compressibility factor of the LJ chains of length $m=16$. Lines and symbols have the same meaning as in Fig. 6.

ical molecules.

CONCLUSIONS

We performed constant temperature molecular dynamics simulations for the freely jointed LJ chains, and obtained their thermodynamic properties from time averages of the corresponding microscopic properties. For the repulsive LJ chains, the compressibility factor from the TPT1 theory agrees well with the simulation results especially at high densities, and the TPT1 theory well accounts for the temperature effects on the compressibility factor. However, the theory slightly overestimates the compressibility factor at low and intermediate densities, which has been also observed for hard-sphere chain

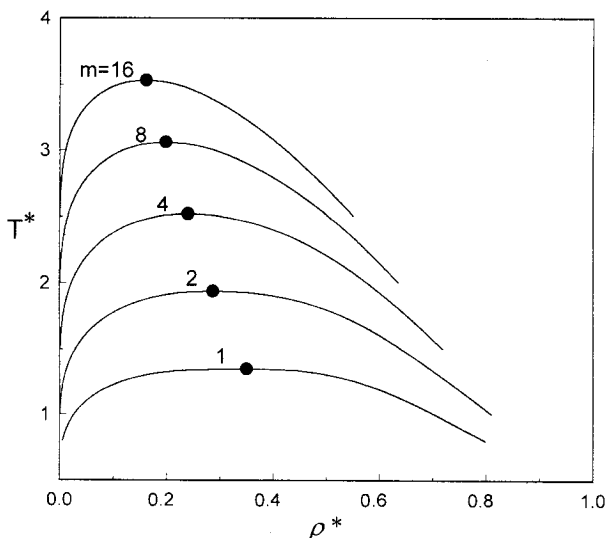


Fig. 8. The vapor-liquid coexisting curves for the LJ chain fluids, calculated from the TPT1-PY equation of state. Solid symbols indicate the critical points.

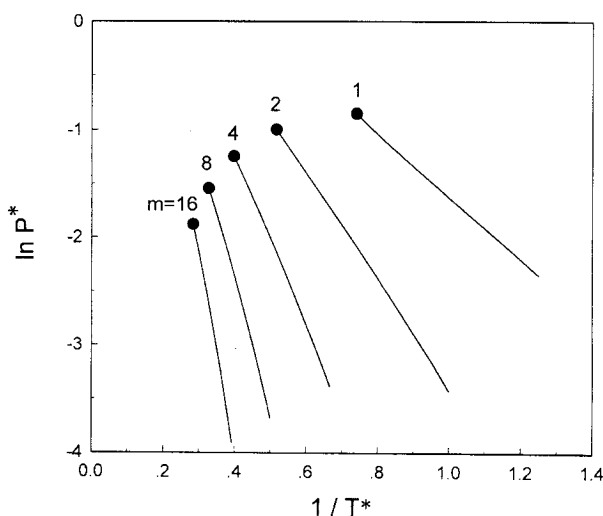


Fig. 9. The vapor pressures of the LJ chain fluids, calculated from the TPT1-PY equation of state. The reduced pressure is defined as $p^* = p\sigma^3/\epsilon$. Solid symbols indicate the critical points.

fluids, because the effect of intramolecular interactions is not taken into account in the TPT1 theory. For the full LJ chains, the TPT1-PY theory is good at low densities and reasonable at high densities, whereas the TPT1-WCA theory is accurate at high densities. This contrast is inevitably due to the accuracy of the methods for obtaining the RDF of the LJ spheres. The vapor-liquid equilibria of the LJ chains are predicted from the TPT1-PY equation of state, and the physically consistent behaviors of the phase envelope and the vapor pressure with increasing chain length are predicted while a more quantitative test awaits Gibbs ensemble simulation data.

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NOMENCLATURE

- A : Helmholtz energy
- $f_{i\alpha}, F_{i\alpha}$: force
- g : radial distribution function
- K : kinetic energy
- k_B : Boltzmann's constant
- l : bond distance
- m : chain length
- $m_{i\alpha}$: mass of segment
- N : number of chains
- P : pressure
- Q : thermal inertia parameter
- r : distance
- $r_{i\alpha}$: position vector
- T : temperature
- U : configurational energy
- u : intermolecular potential
- V : volume
- y : cavity correlation function
- Z : compressibility factor

Greek Letters

- α, β : indices for segments
- ϵ : energy parameter
- η : effective packing fraction
- ξ : friction coefficient
- ρ : number density
- σ : size parameter

Subscripts

- HS : hard sphere
- LJ : Lennard-Jones potential
- RLJ : repulsive Lennard-Jones potential
- ref : reference system
- c : chain fluid
- r : residual property
- *

REFERENCES

- Allen, M. P. and Tildesley, D. J., "Computer Simulation of Liquids", Clarendon Press, Oxford (1987).
- Andersen, H. C., "Rattle: a 'Velocity' Version of the Shake Algorithm for Molecular Dynamics Calculation", *J. Comput. Phys.*, **52**, 24 (1983).
- Banaszak, M., Chiew, Y. C., O'Lenick, R. and Radosz, M., "Thermodynamic Perturbation Theory: Lennard-Jones Chains", *J. Chem. Phys.*, **100**, 3803 (1994).
- Chang, J. and Sandler, S. I., "An Equation of State for the Hard-sphere Chain Fluid: Theory and Monte Carlo Simulation", *Chem. Eng. Sci.*, **49**, 2777 (1994).
- Chapman, W. G., Jackson, G. and Gubbins, K. E., "Phase Equilibria of Associating Fluids. Chain Molecules with Multiple Bonding Sites", *Mol. Phys.*, **65**, 1057 (1988).

- Chapman, W. G., Gubbins, K. E., Jackson, G. and Radosz, M., "New Reference Equation of State for Associating Liquids", *Ind. Eng. Chem. Res.*, **29**, 1709 (1990).
- Gao, J. and Weiner, J. H., "Contribution of Covalent Bond Force to Pressure in Polymer Melts", *J. Chem. Phys.*, **91**, 3168 (1989).
- Ghonasgi, D. and Chapman, W. G., "A New Equation of State for Hard Chain Molecules", *J. Chem. Phys.*, **100**, 6633 (1994).
- Honnell, K. G. and Hall, C. K., "A New Equation of State for Athermal Chains", *J. Chem. Phys.*, **90**, 1841 (1989).
- Hoover, W. G., "Canonical Dynamics: Equilibrium Phase-space Distributions", *Phys. Rev.*, **A31**, 1695 (1985).
- Huang, S. H. and Radosz, M., "Equation of State for Small, Large, Polydisperse and Associating Molecules", *Ind. Eng. Chem. Res.*, **29**, 2284 (1990).
- Johnson, J. K., Muller, E. A. and Gubbins, K. E., "Equation of State for Lennard-Jones Chains", *J. Phys. Chem.*, **98**, 6413 (1994).
- Lee, L. L., "Molecular Thermodynamics of Nonideal Fluids", Butterworths (1988).
- Li, X. and Chiew, Y. C., "Monte Carlo Simulation of Equation of State and Structure of Chain Fluids", *Chem. Eng. Sci.*, **49**, 2805 (1994a).
- Li, X. and Chiew, Y. C., "Monte Carlo Simulation of Lennard-Jones Chains", *J. Chem. Phys.*, **101**, 2522 (1994b).
- Nicolas, J. J., Gubbins, K. E., Streett, W. B. and Tildesley, D. J., "Equation of State for the Lennard-Jones Fluid", *Mol. Phys.*, **37**, 1429 (1979).
- Nose, S., "A Molecular Dynamics Method for Simulations in the Canonical Ensemble", *Mol. Phys.*, **52**, 255 (1984).
- Panagiotopoulos, A. Z., "Direct Determination of Phase Coexistence Properties of Fluids by Monte Carlo Simulation in a New Ensemble", *Mol. Phys.*, **61**, 813 (1987).
- Ryckaert, J. P., Ciccotti, G. and Berendsen, H. J. C., "Numerical Integration of the Cartesian Equation of Motion of a System with Constraints: Molecular Dynamics of n-Alkanes", *J. Comput. Phys.*, **23**, 327 (1977).
- Tavares, F. W., Chang, J. and Sandler, S. I., "Equation of State for the Square-well Chain Fluid Based on the Dimer-version of Wertheim's Perturbation Theory", *Mol. Phys.*, **86**, 1451 (1995).
- Verlet, L. and Weis, J. J., "Equilibrium Theory of Simple Liquids", *Phys. Rev.*, **A5**, 939 (1972).
- Weeks, J. D., Chandler, D. and Andersen, H. C., "Role of Repulsive Forces in Determining the Equilibrium Structure of Simple Fluids", *J. Chem. Phys.*, **54**, 5237 (1971).
- Wertheim, M. S., "Fluids with Highly Directional Attractive Forces. I. Statistical Thermodynamics", *J. Stat. Phys.*, **35**, 19 (1984a).
- Wertheim, M. S., "Fluids with Highly Directional Attractive Forces. II. Thermodynamic Perturbation Theory and Integral Equations", *J. Stat. Phys.*, **35**, 35 (1984b).
- Wertheim, M. S., "Fluids with Highly Directional Attractive Forces. III. Multiple Attraction Sites", *J. Stat. Phys.*, **42**, 459 (1986a).
- Wertheim, M. S., "Fluids with Highly Directional Attractive Forces. IV. Equilibrium Polymerization", *J. Stat. Phys.*, **42**, 477 (1986b).
- Wertheim, M. S., "Thermodynamic Perturbation Theory of Polymerization", *J. Chem. Phys.*, **87**, 7323 (1987).