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Equation of state for hard-sphere chain molecules

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Abstract

An equation of state for homonuclear chain molecules is formulated on the basis of thermodynamic perturbation theory of Wertheim. It yields a very accurate prediction of the compressibility factor of different chain molecules including hard spheres and hard dumbbells as well as flexible chains with up to 200 bonds in a molecule. In addition, a large number of molecular simulation results are used to test the thermodynamic first-order perturbation theory (TPT1), the thermodynamic second-order perturbation theory (TPT2), the scaled particle theory (SPT), the Percus–Yevick and Carnahan–Starling (PY–CS) equation, the generalized Flory–Dimer equation (GF–D) and our equation. For short chain molecules ($m \leq 4$), good agreement between the calculated and computer simulation data can be obtained from all of the above equations, but for long chain molecules the equation proposed in this work is better than the other equations.

Keywords Theory, Equation of state, Hard-sphere chain molecule; Molecular simulation

1. Introduction

Real molecules are usually polyatomic except for the noble gases and metals, so it is important to develop equations of state for chain molecules. Simple models of chain molecules which take into account the repulsive forces between molecules are invariably based on repulsive hard-core potentials. A commonly used model is that of the athermal hard-sphere chain or freely jointed tangent spheres. This simple model can be used as a repulsive potential reference system. Once the thermodynamic properties of the hard-sphere chain molecules are known, the properties of realistic polymers can be obtained by using perturbation theory to consider the effects of the attractive forces in the usual way.

Wertheim (1987) introduced two equations of state for the hard-sphere chain fluid based on his thermodynamic perturbation theory (TPT) (Wertheim, 1984a, b, 1986a, b) of polymerization.

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On the basis of the results of Wertheim and of Jackson et al. (1988), Boublik et al. (1990) formulated an equation of state for fluids of fused hard-sphere bodies. It is an extension of the general form of the equation of state that follows from the scaled particle theory (SPT). The generalized Flory–Dimer theory (GF–D) (Honell and Hall, 1989) is derived as a generalization of the well-known Flory (1942) lattice theory to continuous space. Chiew (1990) derived analytical expressions for an equation of state for the hard-sphere chain fluid based on the “particle–particle” Ornstein–Zernike integral equation in the Percus–Yevick (PY) approximation.

In this paper an equation of state is proposed on the basis of the thermodynamic perturbation theory of Wertheim (1984a, b, 1986a, b). This equation can be applied to systems of linear molecules and flexible chains. A comparison of several equations of state (TPT1, TPT2, SPT, PY–CS, GF–D and the present equation) is made by using a large number of computer simulation data published in the literature.

2. Theory

The equation of state for the hard-sphere chain fluid can be obtained using a simple perturbation theory of Wertheim for molecules with multiple bonding sites (Wertheim, 1984a, b, 1986a, b). When a chain molecule with sphere number m is formed, a mixture of hard-spheres with different diameters and a chain molecule with sphere number $m - 1$ can be taken as a reference system.

Fig. 1 shows the formation of a hard-sphere molecule in which the number of spheres is m . The bond length is equal to the sum of the radii of two neighboring spheres, i.e. $l_{ij} = (\sigma_i + \sigma_j)/2$. In Fig. 1, only $A_i B_{i+1}$ bonding is allowed. In this system, the compressibility factor of hard spheres and the chain contribution:

$$\frac{P}{\rho kT} = \frac{mP}{\rho_s kT} = mZ^{hs} + mZ^{chain} \tag{1}$$

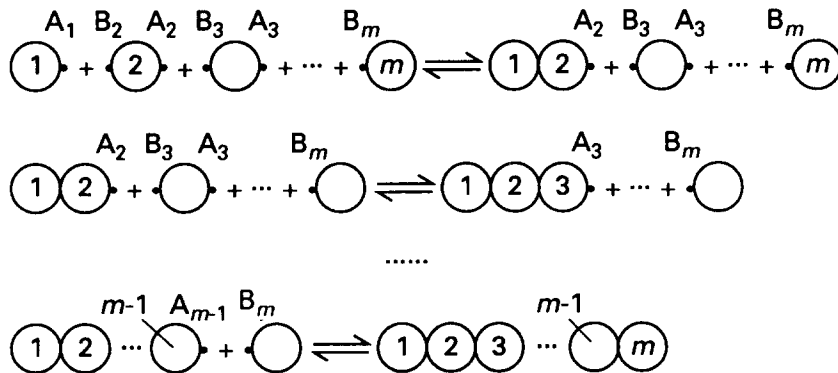


Fig 1 Formation of a chain molecule with $m - 1$ bonds

where the number density of total spheres, ρ_s is equal to $m\rho$, P is the pressure of the system, T is the temperature, ρ is the number density of chain molecules and k is the Boltzmann constant. The term Z^{chain} is given by

$$Z^{\text{chain}} = Z_{12}^{\text{bond}} + Z_{23}^{\text{bond}} + \dots + Z_{m-1 m}^{\text{bond}} = \sum_{i=1}^{m-1} Z_{i,i+1}^{\text{bond}} \quad (2)$$

For the compressibility factor of hard spheres, we can employ the expression of Boublik (1970):

$$Z^{\text{hs}} = \frac{PV}{NkT} = \frac{6}{\pi\rho_s} \left[\frac{\xi_0}{1-\xi_3} + \frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{\xi_2^3(3-\xi_3)}{(1-\xi_3)^3} \right] \quad (3)$$

The reduced densities ξ are defined as

$$\xi_n = \frac{\pi}{6} \sum_i \rho_{s,i} \sigma_i^n \quad (n = 0, 1, 2, 3)$$

When $\sigma_1 = \sigma_2 = \dots = \sigma_m$, Eq. (3) reduces to the Carnahan and Starling equation for pure hard spheres:

$$Z^{\text{hs}} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (4)$$

where $\eta = (\pi/6) \sum_i \rho_{s,i} \sigma_i^3$.

The bonding terms in Eq. (2) is obtained from Jackson et al. (1988):

$$Z_{i,i+1}^{\text{bond}} = \rho_{s,i} \left[\frac{\partial X_{A_i}}{\partial \rho_s} \right]_{T,N} \left[\frac{1}{X_{A_i}} - \frac{1}{2} \right] + \rho_{s,i+1} \left[\frac{\partial X_{B_{i+1}}}{\partial \rho_s} \right]_{T,N} \left[\frac{1}{X_{B_{i+1}}} - \frac{1}{2} \right] \quad (5)$$

where X_{A_i} is the fraction of spheres i unbonded at site A. According to the perturbation theory of Wertheim, X_{A_i} and $X_{B_{i+1}}$ can be expressed as

$$X_{A_i} = \frac{1}{1 + \rho_{s,i+1} X_{B_{i+1}} \Delta_{A_i B_{i+1}}} \quad (6)$$

$$X_{B_{i+1}} = \frac{1}{1 + \rho_{s,i} X_{A_i} \Delta_{A_i B_{i+1}}} \quad (7)$$

For short-range potentials, the function $\Delta_{A_i B_{i+1}}$ is well approximated by Jackson et al. (1988):

$$\Delta_{A_i B_{i+1}} = 4\pi g_{i,i+1}(\sigma_{i,i+1}) \sigma_{i,i+1}^2 \int \langle f_{A_i B_{i+1}}(i, i+1) \rangle_{\omega_i, \omega_{i+1}} dr_{i,i+1} \quad (8)$$

The factor $g_{i,i+1}(\sigma_{i,i+1})$ is the $i-i+1$ contact value of the radial distribution function for the hard-sphere reference mixture with $(\sigma_{i,i+1}) = (\sigma_i + \sigma_{i+1})/2$. The term $\langle f_{A_i B_{i+1}}(i, i+1) \rangle_{\omega_i, \omega_{i+1}} = \langle \exp(-\phi_{A_i B_{i+1}}^{\text{bond}}/kT) - 1 \rangle_{\omega_i, \omega_{i+1}}$ represents an angle average of the Mayer function for the $A_i B_{i+1}$ site-site intermolecular potential over all orientations of spheres i and $i+1$. The integration is over the intermolecular separation $r_{i,i+1}$.

Since only $A_i B_{i+1}$ bonding is allowed, the number of spheres i bonded at A_i must equal the number of spheres $i + 1$ bonded at B_{i+1} :

$$\rho_{s,i}(1 - X_{A_i}) = \rho_{s,i+1}(1 - X_{B_{i+1}}) \quad (9)$$

i.e.

$$X_{B_{i+1}} = 1 - \frac{\rho_{s,i}}{\rho_{s,i+1}}(1 - X_{A_i}) \quad (10)$$

Furthermore, if a pure fluid is formed in the limit of complete bonding we obtain $\rho_{s,1} = \rho_{s,2} = \dots = \rho_{s,m}$. So

$$X_{A_i} = X_{B_{i+1}} = 0$$

After substituting these expressions into Eqs. (6) and (7) and rearranging, we have

$$\lim_{X_{A_i} \rightarrow 0} (\rho_{s,i+1} \Delta_{A_i B_{i+1}} X_{A_i}^2 + X_{A_i} - 1) = 0 \quad (11)$$

$$\lim_{X_{B_{i+1}} \rightarrow 0} (\rho_{s,i} \Delta_{A_i B_{i+1}} X_{B_{i+1}}^2 + X_{B_{i+1}} - 1) = 0 \quad (12)$$

Since $\rho_s = \sum_{i=1}^m \rho_{s,i} = m\rho_{s,i} = m\rho_{s,i+1}$, Eqs. (11) and (12) become

$$\left(\frac{\rho_s \Delta_{A_i B_{i+1}}}{m} \right) X_{A_i}^2 - 1 = 0 \quad (13)$$

$$\left(\frac{\rho_s \Delta_{A_i B_{i+1}}}{m} \right) X_{B_{i+1}}^2 - 1 = 0 \quad (14)$$

i.e.

$$X_{A_i}^2 = X_{B_{i+1}}^2 = \frac{m}{\rho_s \Delta_{A_i B_{i+1}}} \quad (15)$$

Substituting Eq. (15) into Eq. (5), we obtain

$$Z_{i,i+1}^{\text{bond}} = -\frac{1}{m} \left[1 + \frac{\rho_s}{\Delta_{A_i B_{i+1}}} \left(\frac{\partial \Delta_{A_i B_{i+1}}}{\partial \rho_s} \right)_{T,N} \right] \quad (16)$$

The bonding contributions can now be expressed in terms of the contact values of the hard-sphere radial distribution functions:

$$Z_{i,i+1}^{\text{bond}} = -\frac{1}{m} \left\{ 1 + \frac{\rho_s}{g_{i,i+1}(\sigma_{i,i+1})} \left[\frac{\partial g_{i,i+1}(\sigma_{i,i+1})}{\partial \rho_s} \right]_{T,N} \right\} \quad (17)$$

When $i = 1$, the reference system is a hard-sphere mixture system. The contact value of the radial distribution function is

$$g_{12}(\sigma_{12}) = g_{12}^{\text{hs}}(\sigma_{12}) = g^{\text{hs}}(\sigma)$$

Substituting the above equation into Eq. (17), we can obtain

$$Z_{12}^{\text{bond}} = -\frac{1}{m} \left\{ 1 + \rho_s \left[\frac{\partial \ln g^{\text{hs}}(\sigma)}{\partial \rho} \right]_{T,N} \right\} \quad (18)$$

Also let $Z_{12} = mZ_{12}^{\text{bond}}$.

When $2 \leq i \leq m - 1$, the reference system is a mixture of hard spheres and a hard-sphere chain molecule, so

$$\begin{aligned} g_{i,i+1}(\sigma_{i,i+1}) &= g_{i,i+1}^{\text{hs}}(\sigma_{i,i+1}) - \Delta g_{i,i+1}(\sigma_{i,i+1}) \\ &= g^{\text{hs}}(\sigma) - \Delta g(\sigma) \end{aligned}$$

where $\Delta g(\sigma)$ is the difference between radial distribution functions in the hard-sphere mixture and hard-sphere chain mixture.

$$Z_{i,i+1}^{\text{bond}} = -\frac{1}{m} \left\{ 1 + \rho_s \left[\frac{\partial \ln [g^{\text{hs}}(\sigma) - \Delta g(\sigma)]}{\partial \rho_s} \right]_{T,N} \right\} \quad (19)$$

Since

$$\frac{\partial \ln [g^{\text{hs}}(\sigma) - \Delta g(\sigma)]}{\partial \rho_s} = \frac{\partial \ln g^{\text{hs}}(\sigma)}{\partial \rho_s} + \frac{\partial \ln [1 - \Delta g(\sigma)/g^{\text{hs}}(\sigma)]}{\partial \rho_s}$$

we have

$$\begin{aligned} Z_{i,i+1}^{\text{bond}} &= Z_{12}^{\text{bond}} = \frac{Z_{12}}{m} \quad (i = 1) \\ Z_{i,i+1}^{\text{bond}} &= \frac{Z_{12}}{m} - \frac{\rho_s}{m} \frac{\partial \ln [1 - \Delta g(\sigma)/g^{\text{hs}}(\sigma)]}{\partial \rho_s} \quad (2 \leq i \leq m - 1) \end{aligned} \quad (20)$$

By combining the hard-sphere reference term with Eq. (20), the final expression for the molecular compressibility factor is given by

$$Z^{\text{hsc}} = \frac{P}{\rho k T} = mZ^{\text{hs}} + (m - 1)Z_{12} - (m - 2)\rho_s \frac{\partial \ln [1 - \Delta g(\sigma)/g^{\text{hs}}(\sigma)]}{\partial \rho_s} \quad (21)$$

When $m = 2$, the chain molecule becomes the dumbbell molecule and the compressibility factor Z^{DB} of the dumbbell system can be obtained from Eq. (21):

$$Z^{\text{DB}} = 2Z^{\text{hs}} + Z_{12} \quad (22)$$

Z^{DB} can be expressed by the Tildesley–Streett equation (Tildesley and Streett, 1980):

$$Z^{\text{DB}} = \frac{1 + 2.45696\eta + 4.10386\eta^2 - 3.75503\eta^3}{(1 - \eta)^3} \quad (23)$$

We can obtain Z_{12} from Eqs. (22), (23) and (4):

$$Z_{12} = \frac{1 - 0.45696\eta - 2.10386\eta^2 + 1.75503\eta^3}{(1 - \eta)^3} \quad (24)$$

The third term of Eq. (21) is small and it can be regressed from the computer simulation data of chain molecules (Dickman and Hall, 1988; and Gao and Weiner, 1989).

$$\rho_s \frac{\partial \ln[1 - \Delta g(\sigma)/g^{\text{hs}}(\sigma)]}{\partial \rho_s} = \frac{0.75497\eta(1 - 4.6260\eta + 6.3205\eta^2)}{(1 - \eta)^3} \quad (25)$$

From Eqs. (24), (25) and (21), the equation of state for a hard-sphere chain system is obtained:

$$\begin{aligned} \frac{P}{\rho kT} = & m \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - (m - 1) \frac{1 - 0.45696\eta - 2.10386\eta^2 + 1.75503\eta^3}{(1 - \eta)^3} \\ & - (m - 2) \frac{0.75497\eta(1 - 4.6260\eta + 6.3205\eta^2)}{(1 - \eta)^3} \end{aligned} \quad (26)$$

When the above equation is applied to a mixture of hard-sphere chain molecules, m is equal to $\sum_i x_i m_i$, where x_i is the mole fraction of the molecules with sphere number equal to m_i .

Other equations used for hard-sphere chain molecules are listed as follows.

(1) Thermodynamic first-order perturbation theory (TPT1) (Wertheim, 1987):

$$\frac{P}{\rho kT} = m \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - (m - 1) \left[1 - \frac{\eta}{(2 - \eta)} + \frac{3\eta}{(1 - \eta)} \right] \quad (27)$$

(2) Thermodynamic second-order perturbation (TPT2) (Wertheim, 1987):

$$\begin{aligned} \frac{P}{\rho kT} = & m \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - (m - 1) \left[1 - \frac{\eta}{(2 - \eta)} + \frac{3\eta}{(1 - \eta)} \right] \\ & - (m - \tau) \left(1 + \frac{1.284\eta}{1 + 1.284\eta} \right) \end{aligned} \quad (28)$$

where

$$m - \tau = \frac{m}{2} - \frac{m(1 + 4\lambda - 4\lambda/m^2)^{1/2}}{2(1 + 4\lambda)} - \frac{2\lambda}{(1 + 4\lambda)} \quad (29)$$

$$\lambda = 0.233633\eta(1 + 284\eta) \quad (30)$$

(3) Scaled particle theory (SPT) (Boublik et al., 1990):

$$\frac{P}{\rho kT} = \frac{1}{1 - \eta} + \frac{3\alpha\eta}{(1 - \eta)^2} + \frac{\eta^2[(49\alpha - 31) - \eta(11\alpha - 7) - \eta^2(25\alpha - 21)]}{6(1 - \eta)^3} \quad (31)$$

where $\alpha = (m + 1)/2$. In the case of a mixture of chain molecules, α is given by the relationship

$$\alpha = \sum_i x_i m_i / 2 + 1/2$$

(4) Percus–Yevick and Carnahan–Starling (PY–CS) theory (Chiew, 1990):

$$\frac{P}{\rho kT} = m \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - (m - 1) \frac{1 + \eta/2}{(1 - \eta)^2} \quad (32)$$

(5) Generalized Flory–Dimer theory (GF–D) (Honell et al., 1989):

$$\frac{P}{\rho kT} = \left[\frac{V_e(n) - V_e(1)}{V_e(2) - V_e(1)} \right] \left[\frac{1 + 2.45696\eta + 4.10386\eta^2 - 3.75503\eta^3}{(1 - \eta)^3} \right] - \left[\frac{V_e(n) - V_e(2)}{V_e(2) - V_e(1)} \right] \left[\frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \right] \tag{33}$$

where $V_e(1) = 4\pi\sigma^3/3$, $V_e(2) = 9\pi\sigma^3/4$, $V_e(3) = 9.82605\sigma^3$, $V_e(n)$ is estimated from $V_e(n) = V_e(3) + (n - 3)[V_e(3) - V_e(2)]$

3. Results and discussion

Eq. (26) was used to calculate the compressibility factor of hard-sphere chain molecules with different chain lengths and the calculated results are compared with molecular simulation data.

Table 1
Comparison of equations of state from various theories and MC simulation for $m = 2$

η	$P/\rho kT$						
	MC ^a	TPT1	TPT2	SPT	PY–CS	GF–D	This work
0.101	1.75	1.77	1.76	1.77	1.76	1.77	1.77
0.200	3.18	3.17	3.14	3.18	3.09	3.17	3.17
0.312	6.41	6.29	6.24	6.31	6.03	6.30	6.30
0.398	11.16	10.96	10.88	10.97	10.38	10.96	10.96
0.450	15.60	15.61	15.52	15.59	14.72	15.59	15.59
ARD% ^b		1.02	1.48	0.93	4.33	0.97	0.97

^a The MC simulation data are from Archer and Jackson (1991)

^b $ARD\% = \frac{100}{M} \sum_{i=1}^M |Z_i^{cal} - Z_i^{MC}| / Z_i^{MC}$ or $ARD\% = \frac{100}{M} \sum_{i=1}^M |Z_i^{cal} - Z_i^{MD}| / Z_i^{MD}$.

Table 2
Comparison of equations of state from various theories and MC simulation for $m = 3$

η	$P/\rho kT$						
	MC ^a	TPT1	TPT2	SPT	PY–CS	GF–D	This work
0.050	1.42	1.42	1.40	1.42	1.41	1.41	1.38
0.100	2.00	2.00	1.97	2.00	1.97	1.99	1.94
0.300	7.71	7.70	7.57	7.72	7.23	7.64	7.60
0.401	15.23	15.39	15.19	15.40	14.21	15.22	15.17
0.453	21.68	22.31	22.08	22.25	20.49	22.01	21.86
ARD%		0.76	1.49	0.74	4.05	0.71	1.80

^a The MC simulation data are from Amos and Jackson (1991)

The Monte Carlo (MC) data were from Archer and Jackson (1991), Amos and Jackson (1991) and Dickman and Hall (1988). For longer chain systems, more accurate compressibility factor data can be obtained from molecular dynamics (MD) simulation. The MD data were from the

Table 3

Comparison of equations of state from various theories and MC simulation for $m = 4$

η	$P/\rho kT$						
	MC ^a	TPT1	TPT2	SPT	PY-CS	GF-D	This work
0.107	2.25	2.37	2.30	2.37	2.32	2.34	2.23
0.205	4.73	4.88	4.74	4.88	4.63	4.82	4.69
0.252	6.40	6.82	6.64	6.83	6.38	6.73	6.62
0.262	7.46	7.32	7.13	7.33	6.83	7.22	7.12
0.278	8.02	8.19	7.99	8.21	7.62	8.08	7.99
0.289	8.70	8.85	8.64	8.87	8.21	8.73	8.64
0.310	9.80	10.27	10.03	10.29	9.48	10.12	10.04
0.323	10.91	11.25	11.00	11.28	10.36	11.08	11.01
0.340	12.20	12.68	12.42	12.71	11.65	12.49	12.43
0.349	12.70	13.52	13.24	13.55	12.39	13.31	13.25
0.359	13.50	14.51	14.23	14.54	13.28	14.28	14.22
0.376	16.10	16.38	16.08	16.40	14.95	16.11	16.04
0.394	17.80	18.63	18.32	18.65	16.97	18.31	18.22
0.399	18.70	19.31	18.99	19.33	17.58	18.98	18.88
0.410	21.00	20.91	20.58	20.91	19.01	20.54	20.42
0.417	21.70	22.00	21.67	21.99	19.98	21.60	21.47
0.430	24.20	24.23	23.88	24.20	21.98	23.77	23.59
0.437	25.10	25.47	25.12	25.42	23.09	24.98	24.77
ARD% ₀		3.32	1.92	3.40	5.20	2.35	2.06

^a The MC simulation data are from Dickman and Hall (1988)

Table 4

Comparison of equations of state from various theories and MC simulation for $m = 8$

η	$P/\rho kT$						
	MC ^a	TPT1	TPT2	SPT	PY-CS	GF-D	This work
0.066	1.90	2.26	2.15	2.26	2.22	2.21	1.98
0.131	3.79	4.28	4.05	4.27	4.08	4.18	3.82
0.176	5.84	6.40	6.07	6.39	5.99	6.24	5.95
0.227	9.05	9.67	9.24	9.68	8.90	9.44	9.08
0.267	12.43	13.23	12.70	13.25	12.03	12.90	12.60
0.308	17.50	18.09	17.47	18.13	16.29	17.63	17.41
0.332	21.90	21.68	21.00	21.73	19.43	21.12	20.93
ARD% ₀		8.43	4.68	8.41	7.11	6.57	1.69

^a The MC simulation data are from Dickman and Hall (1988)

papers of Denlinger and Hall (1990) and Gao and Weiner (1989). The calculated results from our equation and the computer simulation data for the systems with $m = 2, 3, 4, 8, 16, 32, 51$ and 201 are listed in Tables 1–8. For comparison, the TPT1, TPT2, SPT, PY–CS and GF–D theories were used to calculate the compressibility factors also and the calculated results with the average relative deviation (ARD%) are listed in Tables 1–8 also.

Table 5
Comparison of equations of state from various theories and computer simulation for $m = 16$

η	$P/\rho kT$						
	MC, MD ^a	TPT1	TPT2	SPT	PY–CS	GF–D	This work
0.080	3.76 ^b	4.03	3.73	4.02	3.89	3.90	3.28
0.100	4.23 ^b	5.13	4.75	5.12	4.90	4.96	4.23
0.105	4.67	5.43	5.03	5.42	5.17	5.25	4.50
0.148	7.32 ^b	8.56	7.96	8.55	7.99	8.28	7.40
0.157	8.44	9.35	8.71	9.34	8.69	9.05	8.15
0.200	12.50	13.92	13.06	13.91	12.72	13.48	12.58
0.205	13.20 ^b	14.48	13.60	14.48	13.21	14.02	13.14
0.209	14.15	15.06	14.16	15.06	13.72	14.59	13.71
0.231	15.90 ^b	18.20	17.18	18.21	16.46	17.63	16.80
0.247	19.10	20.80	19.71	20.83	18.73	20.16	19.39
0.247	18.20 ^b	20.80	19.71	20.83	18.73	20.16	19.39
0.262	22.59	23.54	22.37	23.58	21.10	22.81	22.08
0.272	24.10	25.47	24.24	25.51	22.78	24.68	23.99
0.314	34.83	35.67	34.22	35.75	31.60	34.54	34.04
0.367	52.25	53.89	52.16	53.96	47.31	52.10	51.67
0.419	77.09	80.61	78.59	80.46	70.34	77.73	76.75
0.471	111.76	121.23	118.92	120.31	105.45	116.50	113.35
ARD%		9.79	4.21	9.71	5.91	6.34	2.75

^a The MC simulation data are from Dickman and Hall (1988); MD simulation data are from Denlinger and Hall (1990) and Gao and Weiner (1989)

^b MC simulation data.

Table 6
Comparison of equations of state from various theories and MD simulation for $m = 32$

η	$P/\rho kT$						
	MD ^a	TPT1	TPT2	SPT	PY–CS	GF–D	This work
0.100	7.08	8.98	8.16	8.95	8.50	8.62	7.05
0.200	23.00	26.19	24.38	26.18	23.72	25.25	23.33
0.250	37.00	40.80	38.44	40.85	36.37	39.37	37.73
0.300	57.60	61.77	58.86	61.91	54.41	59.62	58.42
ARD%		14.55	6.83	14.54	7.59	10.35	1.30

^a The MD simulation data are from Denlinger and Hall (1990)

Table 7

Comparison of equations of state from various theories and MD simulation for $m = 51$

η	$P/\rho kT$						
	MD ^a	TPT1	TPT2	SPT	PY-CS	GF-D	This work
0.105	11.46	14.48	13.07	14.43	13.61	13.85	11.22
0.157	23.04	26.59	24.35	26.54	24.38	25.53	22.39
0.195	34.87	38.89	36.01	38.86	35.14	37.41	34.26
0.243	56.56	60.15	56.44	60.22	53.54	57.96	55.18
0.309	101.04	104.60	99.68	104.82	91.64	100.79	98.96
0.340	130.17	134.21	128.71	134.47	116.94	129.25	127.74
0.367	160.56	166.28	160.28	166.47	144.33	160.00	158.48
0.419	238.12	250.60	243.62	250.07	216.37	240.53	237.10
0.471	346.51	379.05	371.10	375.95	326.45	362.56	351.56
ARD%		9.39	3.92	9.25	8.36	5.38	1.80

^a The MD simulation data are from Gao and Weiner (1989)

Table 8

Comparison of equations of state from various theories and MD simulation for $m = 201$

η	$P/\rho kT$						
	MD ^a	TPT1	TPT2	SPT	PY-CS	GF-D	This work
0.105	36.80	53.26	47.54	53.07	49.78	50.72	40.04
0.157	79.44	100.46	91.39	100.24	91.64	96.16	83.40
0.209	152.11	169.85	157.21	169.82	151.99	163.11	150.57
0.262	256.20	273.56	257.11	273.97	241.10	263.10	252.84
0.314	407.16	422.85	402.55	423.76	368.52	406.70	399.52
0.367	621.54	647.96	623.66	648.66	560.14	622.41	616.24
0.419	927.79	979.13	950.89	976.95	842.21	938.25	924.32
0.471	1354.76	1484.03	1451.87	1471.58	1273.63	1417.13	1372.45
ARD%		14.10	7.38	13.92	11.40	9.35	2.57

^a The MD simulation data are from Gao et al (1989)

From Tables 1–3, it can be seen that for short chain molecules good agreement between the calculated and computer simulation values are obtained for TPT1, TPT2, SPT, GF-D and our equation, but Tables 4–8 indicate that for long chain molecules the results of our equation are better than those calculated from the other theories; even the results of TPT2 are more accurate than those of TPT1.

Fig. 2 gives the relative deviation in compressibility factor for the chain molecule with $m = 201$ calculated from six theories. When η is small ($\eta < 0.2$), the deviations between the five equations (TPT1, TPT2, SPT, PY-CS, GF-D) and the computer simulation data are very large. When η becomes bigger, TPT2, GF-D and our equation gives good results; TPT1 and

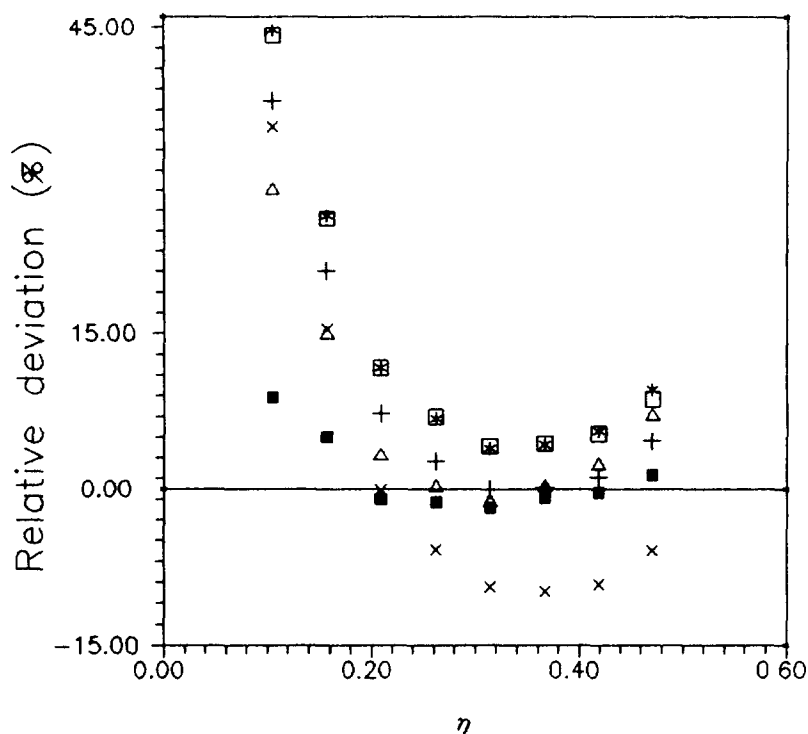


Fig. 2. Comparison of the relative deviation in compressibility factor for the chain molecule with $m = 201$ calculated from six theories: *, TPT1, Δ , TPT2, \square , SPT, \times , PY-CS, +, GF-D; \blacksquare , this work

SPT give higher results; the PY-CS equation yields much lower results than the computer simulation data. Over the whole range of η , only our equation gives small relative deviations.

Table 9 shows the comparison between theoretical and computer simulation data for compressibility factors of equimolar mixtures of dumbbells and tetraatomic molecules. In Table 10, a comparison between theoretical and computer simulation values of the compressibility factor is given for hard spheres and homonuclear dumbbells at three different mole fractions, x_2 . The error in the computer simulation data is estimated to be 3%. It is evident that the theoretical

Table 9
Compressibility factor of equimolar mixtures of dumbbells and tetra-atomic molecules

η	$P/\rho kT$					
	MC ^a	TPT1	TPT2	SPT	PY-CS	This work
0.200	3.94	3.94	3.86	3.94	3.78	3.85
0.300	7.70	7.70	7.57	7.72	7.23	7.60
0.350	10.65	10.81	10.65	10.84	10.06	10.68
ARD%		0.52	1.29	0.70	5.25	1.32

^a The MC simulation data are from Boublik et al (1990).

Table 10

Compressibility factor of binary mixtures of hard spheres(1) and homonuclear hard dumbbells(2)

η	X_2	$P/\rho kT$					
		MC ^a	TPT1	TPT2	SPT	PY-CS	This work
0.35	0.25	5.95	5.91	5.90	5.92	5.81	5.91
0.43	0.25	9.74	9.62	9.61	9.63	9.43	9.62
0.30	0.50	4.88	4.91	4.89	4.92	4.79	4.91
0.43	0.50	11.06	10.94	10.91	10.95	10.57	10.94
0.35	0.75	7.26	7.31	7.26	7.33	7.02	7.31
0.43	0.75	12.31	12.27	12.21	12.27	11.70	12.27
ARD%			0.77	1.03	0.76	3.34	0.80

^a The MC simulation data are from Wojcik and Gubbins (1983)

compressibility factors calculated from TPT1, TPT2, SPT and our equation are in accord with the computer simulation data. Tables 9 and 10 demonstrate that the proposed equation predicts the behavior of these simple mixtures very well.

4. Conclusions

Based on the thermodynamic perturbation theory of Wertheim, the equation of state for a hard-sphere chain system is presented. It is shown that this equation of state yields accurate prediction of the compressibility factors of different molecular models including hard spheres and hard dumbbells as well as flexible chains with up to 200 bonds in a molecule.

Acknowledgment

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List of symbols

g	radial distribution function
k	Boltzmann constant
l	bond length
m	number of spheres in a chain molecule
M	experimental point
N	total number of spheres
P	pressure (Pa)
T	absolute temperature (K)
x	mole fraction of chain molecule
X	fraction of spheres unbonded

Greek letters

α	parameter of non-sphericity
η	packing fraction of hard chains
ξ	reduced density
ρ	number density of hard-sphere chain molecules (nm^{-3})
ρ_s	number density of total hard spheres (nm^{-3})
$\rho_{s,i}$	number density of hard sphere i (nm^{-3})
σ	hard-sphere diameter (nm)

Superscripts

cal	calculation
DB	dumbbells
hs	hard sphere
hsc	hard-sphere chain
MC	Monte Carlo simulation
MD	molecular dynamics simulation

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