









and it predicts the thermodynamic properties of the hard-sphere pure fluid with the same accuracy as the computer simulation techniques. Accordingly the terms  $A_0$  and  $kt(\partial\rho/\partial p)_T^0$  given by eqn (27) is quite reliable.

The major inaccuracy in the perturbation equation of state, eqn (12), is the approximations involved in  $G(\eta, s)$  and  $g_0^{(1)}(\eta, y)$ . As it was mentioned before these two functions are the results of the Percus–Yevick approximation theory [6].

These functions which appear to be the closest values to the respective results of simulation studies, become quite unsatisfactory for very dense states. In order to correct the Percus–Yevick result of the hard-sphere radial distribution function Verlet and Weis [8] proposed the following relation for the hard-sphere radial distribution function

$$g_0(\eta, y) = g_0^{PY}(\theta, y) + \delta g_0(\theta, y) \tag{28}$$

such that

$$\delta g_0(\theta, y) = \left(\frac{B}{y}\right) e^{-\mu(y-1)} \cos [\mu(y-1)], \tag{29}$$

$$B = \frac{3}{4} \frac{\theta^2(1 - 0.7170 - 0.114\theta^2)}{(1 - \theta)^4}, \tag{29-1}$$

$$\mu = \frac{24B}{\theta g_0^{PY}(\theta, 1)}, \tag{29-2}$$

and

$$\theta = \eta \left(1 - \frac{n}{16}\right). \tag{29-3}$$

In eqn (28), the term  $g_0^{PY}(\theta, y)$  stands for the hard-sphere radial distribution function derived through the Percus–Yevick approximation theory when  $\eta$  is replaced with  $\theta$ .

With the consideration of eqn (28) for the radial distribution of the hard-sphere reference system the perturbation equation of state will be in the following form (9)

$$\begin{aligned} \frac{A - A^{id}}{NkT} = & \frac{(4 - 3\eta)\eta}{(1 - \eta)^2} + \frac{6\eta}{T^*} \left\{ 2[J_1(\theta, c) - J_2(\theta, c) + J_5(\theta, c)] \right. \\ & \left. - kT \left(\frac{\partial\rho}{\partial p}\right)_T^0 \frac{1}{T^*} [J_3(\theta, c) - J_4(\theta, c) + J_6(\theta, c)] \right\}. \end{aligned} \tag{30}$$

In the above equation  $J_1, J_2, J_3$  and  $J_4$  are the same as eqns (13)–(16) except that wherever  $\eta$  appears in eqns (13)–(16), it should be replaced by  $\theta$  which is given by eqn (29-3). The relations for  $J_5$  and  $J_6$  are as the following

$$J_5(\theta, c) = \int_{1/c}^{\infty} \delta g_0(\theta, y) u^*(c, y) y^2 dy \tag{31}$$

and

$$J_6(\theta, c) = \int_{1/c}^{\infty} \delta g_0(\theta, y) u^{*2}(c, y) y^2 dy. \tag{32}$$

Equation (30) together with its auxiliary relations comprises the improved perturbation equation of state of pure fluids with the consideration of pair-wise potentials for the intermolecular potential function.

The assumption of pair-wise additivity of the total intermolecular potential energy function for a system of interacting particles which is in a condensed state are too drastic [2, 10]. The research efforts by several investigators have proved that for the prediction of the thermodynamic properties of real fluids through molecular approaches one should consider both

two- and three-body intermolecular potentials[11, 12]. It is shown that the triple-dipole interaction potential is the dominant three-body potential, at least, for simple molecules[12]. A relation for triple-dipole interaction is derived through the quantum theory by Axilrod and Teller[13] as follows

$$w_{123}^{\text{disp}} = \nu \frac{1 + 3 \cos \alpha_1 \cos \alpha_2 \cos \alpha_3}{(r_{12}r_{13}r_{23})^3}. \quad (33)$$

In the above relation  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  are the angles, and  $r_{12}$ ,  $r_{13}$  and  $r_{23}$  are the sides of the triangle formed by particles 1, 2 and 3 and  $\nu$  is a parameter which is defined by the following relation for interaction of identical particles[13]

$$\nu = \frac{9}{16} I \alpha^3, \quad (34)$$

where  $I$  and  $\alpha$  are the ionization potential and the molecular polarizability respectively. In the case when both two- and three-body interaction potentials are considered for the total potential energy function of the fluid one should add the following term to the right-hand side of the perturbation equation of state introduced by eqn (30)

$$\frac{A_{3b}}{NkT} = \frac{\nu \rho^2 d^6}{6kT} \iint g_0(123) w_{123}^{\text{disp}} dr_2 dr_3. \quad (35)$$

The above equation is the first-order perturbation term due to the three-body interactions[4]. Barker *et al.* have derived the following analytic form for  $A_{3b}/NkT$  through a computer simulation calculation[14].

$$\frac{A_{3b}}{NkT} = \frac{\nu \eta^2}{kTd^9} \frac{9 \cdot 87748 + 11 \cdot 76739 \eta - 4 \cdot 20027 \eta^2}{1 - 1 \cdot 12789 \eta + 0 \cdot 73166 \eta^2}. \quad (36)$$

This relation is found to have an accuracy of one part in  $10^5$  when it is compared with the direct results of computer simulation calculations[14].

By adding  $A_{3b}/NkT$  to the right-hand side of eqn (30) one will be able to consider the two- and three-body potential energy functions in the prediction of thermodynamic properties of fluids through the perturbation equation of state.

#### RESULTS AND DISCUSSION

With the availability of the relation for the Helmholtz free energy one may calculate compressibility, internal energy, and the Gibbs free energy through the following thermodynamic relations:

Compressibility: 
$$\frac{p}{\rho kT} = 1 + \rho \frac{\partial}{\partial \rho} \left( \frac{A - A^{id}}{NkT} \right)_{T,N}$$

Internal energy: 
$$\frac{U_i - U_i^{id}}{NkT} = -T \frac{\partial}{\partial T} \left( \frac{A - A^{id}}{NkT} \right)_{\rho,N}$$

Gibbs free energy: 
$$\frac{G - G^{id}}{NkT} = \frac{A - A^{id}}{NkT} + \frac{P}{\rho kT} - 1.$$

In order to evaluate the perturbation equation of state developed here, in the first step it is necessary to compare the thermodynamic properties calculated by this equation of state with the results of the molecular simulation techniques. The simulation techniques have been successful in predicting not only the thermodynamic properties of hard-sphere fluid, but also the properties of fluids possessing Lennard-Jones intermolecular potential energy function[15]. The comparison of the results of the perturbation equation of state with the computer simulation calculations will be free from the complexities which would exist in the case of comparison of the perturbation results with the experimental thermodynamic properties. This is due to the *a priori*

assumption of the form of the two body intermolecular potential function and the non-existence of the many-body interaction potentials in the simulation studies.

The compressibility, the Helmholtz free energy, and the internal energy of a fluid with Lennard-Jones intermolecular potential function as it is calculated through the Monte Carlo simulation technique [15] are reported in Table 1 for different reduced temperatures,  $kT/\epsilon$ , and reduced densities,  $\rho\sigma^3$ . Also reported on Table 1 are the thermodynamic properties calculated through the original perturbation equation of state, eqn (12), and the corrected perturbation

Table 1. Compressibility, Helmholtz free energy, and internal energy of Lennard-Jones fluid for different isotherms

$\rho^*$	$Z^a$	$Z^b$	$Z^c$	$\left[\beta \frac{A - A^{id}}{N}\right]^a$	$\left[\beta \frac{A - A^{id}}{N}\right]^b$	$\left[\beta \frac{A - A^{id}}{N}\right]^c$	$U_i^a$	$U_i^b$	$U_i^c$
<b><math>T^* = 0.75</math></b>									
0.1	0.23	0.31	0.30	-0.80	-0.73	-0.73	-1.15	-0.82	-0.82
0.2	-0.29	-0.30	-0.31	-1.48	-1.40	-1.41	-1.90	-1.55	-1.56
0.3	-0.78	-0.85	-0.87	-2.10	-2.03	-2.05	-2.58	-2.25	-2.25
0.4	-1.20	-1.32	-1.34	-2.68	-2.63	-2.65	-3.21	-2.93	-2.93
0.5	-1.69	-1.63	-1.65	-3.22	-3.19	-3.21	-3.73	-3.60	-3.61
0.6	-2.05	-1.65	-1.67	-3.73	-3.67	-3.70	-4.36	-4.27	-4.26
0.7	-1.71	-1.19	-1.23	-4.17	-4.05	-4.09	-5.09	-4.92	-4.90
0.8	-0.53	0.03	-0.08	-4.47	-4.28	-4.32	-5.78	-5.52	-5.47
<b><math>T^* = 1.15</math></b>									
0.1	0.61	0.65	0.64	-0.38	-0.37	-0.73	-0.86	-0.73	-0.73
0.2	0.35	0.34	0.33	-0.73	-0.71	-0.72	-1.55	-1.41	-1.42
0.3	0.12	0.09	0.08	-1.05	-1.03	-1.04	-2.24	-2.08	-2.09
0.4	-0.09	-0.07	-0.10	-1.34	-1.31	-1.33	-2.85	-2.75	-2.75
0.5	-0.13	-0.08	-0.12	-1.59	-1.56	-1.58	-3.47	-3.41	-3.41
0.6	0.07	0.17	0.10	-1.78	-1.71	-1.77	-4.14	-4.06	-4.05
0.65	0.31	0.42	0.35	-1.84	-1.79	-1.83	-4.45	-4.37	-4.36
0.75	0.75	1.17	1.33	1.19	-1.89	-1.82	-1.87	-5.13	-5.12
<b><math>T^* = 2.74</math></b>									
0.1	0.97	0.97	0.97	-0.03	-0.03	-0.03	-0.61	-0.60	-0.57
0.2	0.99	0.99	0.98	-0.05	-0.05	-0.05	-1.21	-1.19	-1.19
0.3	1.04	1.06	1.04	-0.05	-0.04	-0.05	-1.78	-1.77	-1.78
0.4	1.20	1.21	1.18	-0.01	-0.01	-0.02	-2.37	-2.35	-2.36
0.55	1.65	1.68	1.62	0.06	0.12	0.09	-3.21	-3.18	-3.19
0.7	2.64	2.65	2.50	0.37	0.38	0.33	-3.90	-3.88	-3.90
0.8	3.60	3.73	3.47	0.65	0.68	0.59	-4.28	-4.21	-4.23
<b><math>T^* = 1.35</math></b>									
0.1	0.72	0.73	0.73	-0.29	-0.28	-0.28	-0.78	-0.70	-0.70
0.2	0.50	0.51	0.51	-0.56	-0.53	-0.54	-1.51	-1.37	-1.37
0.3	0.35	0.35	0.33	-0.80	-0.76	-0.77	-2.09	-2.02	-2.03
0.4	0.27	0.27	0.24	-1.00	-0.97	-0.98	-2.75	-2.68	-2.69
0.5	0.30	0.34	0.30	-1.16	-1.12	-1.15	-3.37	-3.33	-3.34
0.55	0.41	0.46	0.41	-1.22	-1.18	-1.21	-3.70	-3.65	-3.65
0.7	1.17	1.33	1.21	-1.29	-1.23	-1.28	-4.68	-4.56	-4.55
0.8	2.42	2.55	2.33	-1.19	-1.11	-1.18	-5.25	-5.09	-5.06

<sup>a</sup> "Exact" Monte Carlo values [15].

<sup>b</sup> Without the correction of  $g_o(r, d)$ : eqn (12).

<sup>c</sup> With the correction of  $g(r, d)$ : eqn (30).

Table 2. Intermolecular potential parameters of Kihara pair potential function and Axilrod-Teller Triple-dipole potential function

	Argon	Methane	Neopentane
$\sigma$ ( $^{\circ}\text{A}$ )	3.314	3.620	5.785
[Ref. (17)]			
$\epsilon/k$ ( $^{\circ}\text{K}$ )	147.20	204.30	554.20
[Ref. (17)]			
$a^* = \gamma/(\sigma - \gamma)$	0.125	0.200	0.550
[Ref. (17)]			
$I$ (eV)	15.96	13.16	10.35
[Ref. (18)]			
$\alpha$ ( $\text{A}^3/\text{mole}$ )	1.6244	2.699	10.14
[Ref. (2)]			
$\nu/k \times 10^{-9}$ ( $\text{A}^9 \cdot ^{\circ}\text{K}$ )	44.669	168.959	7046.54
[eqn (34)]			

Table 3. Experimental and calculated values of the PVT properties of Argon in the vapor-liquid equilibria region. For the two-body potential function the Kihara spherical-core function is used and for the three-body potential function the Axilrod-Teller function is used

P (ATM)	Exptl <sup>a</sup>	T (°K)		Exptl <sup>a</sup>	Specific volume Liquid state		Exptl <sup>a</sup>	(cm <sup>3</sup> /mole) Vapor state	
		Calculated			Calculated			Calculated	
		2-Body potential	2 & 3-Body potential		2-Body potential	2 & 3-Body potential		2-Body potential	2 & 3-Body potential
1.	87.29	91.5	87.04	28.7	26.7	28.2	6999.0	7360.0	6971.0
3.	99.20	104.1	98.90	30.2	28.3	29.8	2533.0	2720.0	2552.0
5.	105.97	111.27	106.63	31.3	29.3	30.9	1578.0	1704.0	1591.0
10.0	116.81	122.77	118.10	33.4	31.1	33.1	802.5	895.0	839.9
15.	124.22	130.65	126.0	35.3	32.7	34.9	529.3	608.6	569.4
20.	130.03	136.90	132.25	37.2	34.0	36.6	383.6	460.0	428.5
30.	139.06	146.73	142.12	42.3	36.8	39.8	233.8	305.9	280.0
Average deviation		5.1%	1.1%		7.9%	2.0%		14.0%	6.5%

<sup>a</sup>Ref. (19).

$$^b \text{Average deviation} = \frac{1}{N} \sum_{i=1}^N \left[ \frac{|X_{\text{Exptl}} - X_{\text{Calc}}|}{X_{\text{Exptl}}} \right] \times 100.$$

Table 4. Experimental and calculated values of PVT properties of Methane in the vapor-liquid equilibria region. For the two-body potential function the Kihara spherical-core function is used and for the three-body potential function the Axilrod-Teller function is used

P (ATM)	Exptl <sup>a</sup>	T (°K)		Exptl <sup>a</sup>	Specific volume Liquid state		Exptl <sup>a</sup>	(cm <sup>3</sup> /mole) Vapor state	
		Calculated			Calculated			Calculated	
		2-Body potential	2 & 3-Body potential		2-Body potential	2 & 3-Body potential		2-Body potential	2 & 3-Body potential
0.881	110.0	110.6	111.9	37.63	31.4	34.8	9958.0	9983.0	10175.0
1.905	120.0	130.1	118.5	38.96	34.8	35.9	4899.0	4980.0	4910.0
2.669	125.0	136.3	127.3	39.68	34.41	36.77	3592.0	4137.0	3708.0
3.641	130.0	141.5	132.5	40.44	34.57	37.45	2684.0	3019.0	2790.0
6.339	140.0	152.0	142.9	42.17	35.84	39.08	1576.0	1810.0	1671.0
10.270	150.0	162.5	153.3	44.40	37.34	40.97	981.5	1153.0	1062.0
15.740	160.0	173.1	163.8	47.31	39.09	43.25	630.7	767.9	703.2
23.000	170.0	183.6	173.2	51.14	41.18	45.80	411.7	530.0	476.7
Average deviation		7.3%	2.0%		16.0%	8.0%		15.8%	7.2%

<sup>a</sup>Ref. (20).

Table 5. Experimental and calculated values of the PVT properties of Neopentane in the vapor-liquid equilibria region. For the two-body potential function the Kihara spherical-core function is used and for the three-body potential function the Axilrod-Teller function is used

P (ATM)	Exptl <sup>a</sup>	T (°K)		Exptl <sup>a</sup>	Specific volume Liquid state		Exptl <sup>a</sup>	(cm <sup>3</sup> /mole) Vapor state	
		Calculated			Calculated			Calculated	
		2-Body potential	2 & 3-Body potential		2-Body potential	2 & 3-Body potential		2-Body potential	2 & 3-Body potential
7.262	353.2	347.4	342.0	140.1	156.8	160.0	3259.0	3390.0	3321.0
9.002	363.2	358.4	353.0	144.2	160.5	162.1	2611.0	2760.0	2694.0
11.027	373.2	269.0	364.1	149.2	166.3	167.1	2101.0	2300.0	2205.0
13.372	383.2	380.6	375.0	154.6	170.6	171.5	1689.0	1890.0	1817.0
16.068	393.2	393.1	389.5	161.3	175.3	179.1	1360.0	1560.0	1505.0
19.143	403.2	403.1	400.2	169.8	180.6	184.1	1086.0	1290.0	1253.0
22.651	413.2	414.6	410.1	181.3	186.5	192.1	852.4	1070.0	1043.0
26.652	423.2	426.4	420.7	199.8	193.1	206.1	643.3	880.0	886.8
28.858	428.2	432.4	426.6	216.1	197.7	212.1	534.8	793.1	801.2
Average deviation		0.9%	1.5%		8.4%	9.5%		19.4%	17.1%

<sup>a</sup>Ref. (21).

equation of state, eqn (30), with the consideration of Lennard-Jones potential function as the only intermolecular potential energy function. According to Table 1 the results of the corrected perturbation equation of state are generally closer to the Monte Carlo simulation results than the results of the original perturbation equation of state.

In order to examine the corrected perturbation equation of state. Equation (30), for the case of real fluids this equation is used here to predict the properties of argon, methane and neopentane in liquid and vapor states. These three fluids have been chosen for the purpose of demonstrating the extent of the applicability of the perturbation equation of state for the prediction of properties of real fluids. The molecules of argon, methane and neopentane represent a wide spectrum of nonpolar molecules with spherical symmetry. The intermolecular potential parameters of argon, methane and neopentane are reported in Table 2. The experimental PVT properties of argon, methane, and neopentane, along with the predicted values of these properties for different intermolecular potential energies, are reported in Tables 3-5 and in Figs. 1-3. For the calculation of the thermodynamic properties of real fluids the Kihara spherical-core potential function, eqn (23), is used as the pair-interaction potential and the Axilrod-Teller triple-dipole potential function, eqn (33), is used as the three-body potential function. The Kihara sperical-core potential

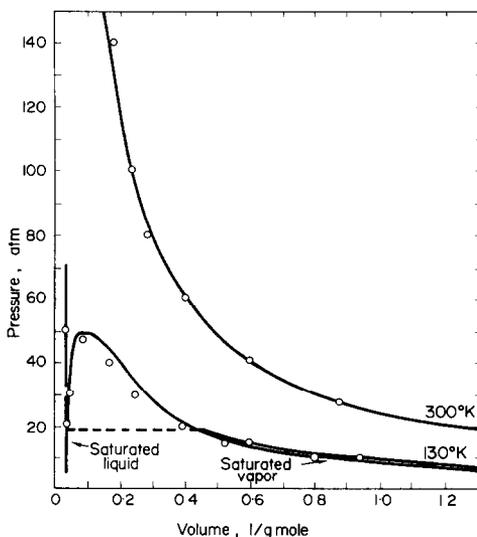


Fig. 1. Pressure-volume-temperature diagram of argon. The calculations are based on the corrected perturbation equation of state, eqn (30), with consideration of both two-body (Kihara) and three-body (Axilrod-Teller) intermolecular potential functions. —, calculated; O, exptl. data Ref. [19].

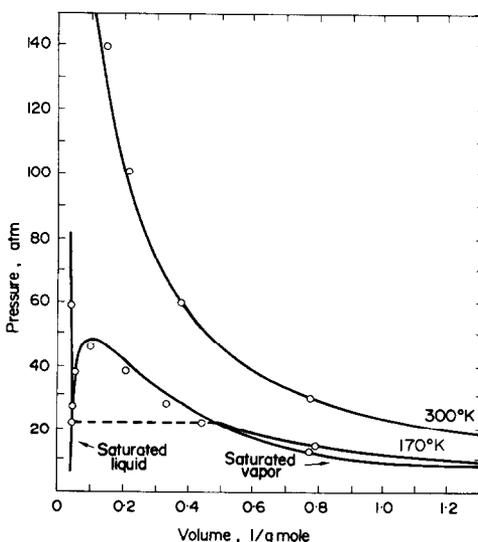


Fig. 2. Pressure-volume-temperature diagram of methane. Potential functions used are the same as in Fig. 1. —, calculated; O, exptl. data Ref. [20].

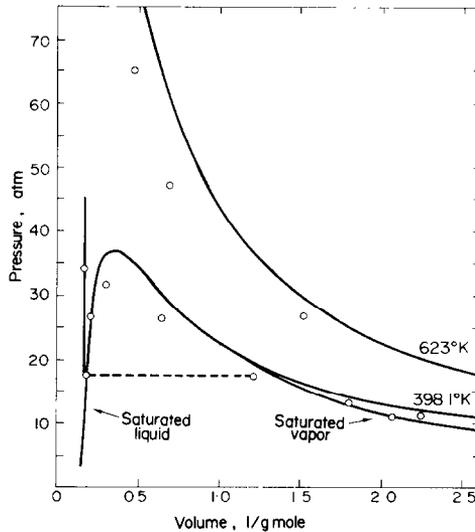


Fig. 3. Pressure-volume-temperature diagram of neopentane. Potential functions used are the same as in Fig. 1. —, calculated; ○, exptl. data Ref. (21).

function is a more realistic-potential function than the Lennard-Jones potential function and as a result it is generally preferred over the Lennard-Jones potential function in the prediction of properties of real fluids[16]. The calculations reported in Tables 3-5 are based on the corrected-perturbation equation of state, eqn (30), with and without the consideration of the three-body potential. In the case when the three-body potential is considered, eqn (36) is added to the right hand side of eqn (30). According to Tables 3-5, the addition of the perturbation term due to the three-body interactions to the perturbation equation of state will greatly improve the predicted values of thermodynamic properties of both liquid and vapor phases, of argon, methane and neopentane. The predicted PVT relations of argon, methane and neopentane through the corrected perturbation equation of state and with the consideration of two- and three-body potentials are also reported in Figs. 1-3.

From the computations presented in this report it may be concluded that the perturbation approach to the equations of state has been quite successful in the prediction of thermodynamic properties of argon, methane, and neopentane in liquid and in vapor states. Also it may be concluded that the contribution of the three-body potential function to the thermodynamic properties of real fluids may not be overlooked. In order to extend the applicability of the perturbation equation of state for the prediction of the properties of dense fluids with more complicated molecules the knowledge about the intermolecular potential functions of these fluids would be essential.

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#### REFERENCES

- [1] G. A. MANSOORI and F. B. CANFIELD, *Ind. Engng Chem.* **62**, 12 (1970).
- [2] J. O. HIRSCHFELDER, C. F. CURTISS and R. B. BIRD, *Molecular Theory of Gases and Liquids*. Wiley, New York (1964).
- [3] R. W. ZWANZIG, *J. chem. Phys.* **22**, 1420 (1954).
- [4] J. A. BARKER and D. HENDERSON, *Ann. Rev. Phys. Chem.* **23** (1972).
- [5] G. A. MANSOORI, J. A. PROVINI and F. B. CANFIELD, *J. chem. Phys.* **51**, 5295 (1969).
- [6] M. S. WERTHEIM, *Phys. Rev. Lett.* **10**, 321 (1963).
- [7] N. F. CARNAHAN and K. E. STARLING, *J. chem. Phys.* **51**, 635 (1969).
- [8] L. VERLET and J. J. WEIS, *Phys. Rev. A* **5**, 939 (1971).
- [9] S. S. LAN, Ph.D. Dissertation, University of Illinois, Chicago, Illinois (1975).
- [10] J. S. ROWLINSON, *Liquids and Liquid Mixtures* 2nd Edn. Butterworth, London (1969).
- [11] J. A. BARKER, D. HENDERSON and W. R. SMITH, *Phys. Rev. Lett.* **21**, 134 (1968).
- [12] I. R. McDONALD and K. SINGER, *Chem. Soc. (London)* **14**, 238 (1970).
- [13] B. M. AXILROD and E. TELLER, *J. chem. Phys.* **17**, 1349 (1949).
- [14] J. A. BARKER, R. A. FISCHER and R. O. WATTS, *Mol. Phys.* **21**, 657 (1971).
- [15] J. P. HANSEN, *Phys. Rev. A* **2**, 221 (1970).

- [16] L. S. TEE, S. GOTOH and W. E. STEWART, *Ind. Engng Chem. Fund.* **5**, 363 (1966).  
 [17] A. E. SHERWOOD and J. M. PRAUSNITZ, *J. chem. Phys.* **41**, 429 (1964).  
 [18] C. D. HODGMAN, *Handbook of Chemistry and Physics*, 53rd Edn. Chemical Rubber Publishing Co., Cleveland, Ohio (1972-1973).  
 [19] F. DIN, *Thermodynamic Functions of Gases*, Vol. 2. Butterworth, London (1961).  
 [20] F. DIN, *Thermodynamic Functions of Gases*, Vol. 3. Butterworth, London (1961).  
 [21] P. P. DAWSON, I. H. SILBERBERG And J. J. McKETTA, *J. chem. Engng Data* **18**, 7 (1973).

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NOMENCLATURE

$a^*$	$\gamma(\sigma - \gamma)$	$w$	triplet-intermolecular potential function
$A$	Helmholtz free energy	$y$	$r/d$
$c$	$d/\sigma$	$Z$	configurational integral
$d$	hard-sphere diameter		
$g$	radial distribution function	<i>Greek Symbols</i>	
$g^{(n)}$	$n$ th distribution function	$\alpha$	polarizability
$G$	Laplace transform of $yg_0(\eta, y)$	$a_i$	angle
$G$	Gibbs free energy	$\gamma$	Kihara spherical-core diameter
$h$	Planck's constant	$\delta g_0$	correction term of $g_0$
$I$	ionization potential	$\epsilon$	energy parameter of pair-potential function
$J_i$	defined by eqns (13)-(16), (31), (32)	$\eta$	$(\pi/6)\rho d^3$
$k$	Boltzmann's constant	$\theta$	$\eta(1 - \eta/16)$
$m$	molecular mass	$\Lambda$	$(h^2/2\pi mkT)^{1/2}$
$N$	number of molecules	$\nu$	parameter of triplet-potential function
$P$	pressure	$\rho$	$N/V$ (number density)
$Q$	partition function	$\sigma$	length parameter of pair-potential function
$r$	intermolecular distance		
$T$	absolute temperature	<i>Subscripts and Superscripts</i>	
$u$	pair-intermolecular potential function	$0$	hard-sphere reference system
$U$	total intermolecular potential function	$*$	dimensionless property
$U_1$	inverse Laplace transform of $yu^*(c, y)$	$i, j$	molecules $i$ and $j$
$U_2$	inverse Laplace transform of $yu^{*2}(c, y)$	$id$	ideal gas
$V$	volume	$P\bar{Y}$	Percus-Yevick