

TEST OF SIMPLE FLUID THEORIES

Stanislav LABÍK and Anatol MALIJEVSKÝ

*Department of Physical Chemistry,
Prague Institute of Chemical Technology, 166 28 Prague 6*

Received September 9th, 1981

The compressibility factors and configuration energies of the Lennard-Jones pair-additive fluid were calculated in terms of the PY, HNC, HTA, ORPA, and EXP approximations, the Lado method and the method by Madden and Fitts. The results were compared with Monte Carlo data. In the gaseous region, the EXP approximation, the Lado method and the method by Madden and Fitts are substantially better than the remaining approaches. The last-mentioned method is the most successful.

The aim of this work is to verify some up-to-date theories of simple fluids in a wide range of temperatures and densities. When testing them, we can bear in mind either the ability of theory to describe the system structure or its thermodynamic behaviour. The comparison of calculated radial distribution function (RDF) with simulated data is a direct test of structure. However, such a test is of little practicality for a large region of the temperature-density surface: Partly the reliable simulated data are not available in a sufficient extent, partly the results would be too extensive. We assume that a suitable indirect test of RDF is the comparison of the simulated compressibility factors, z , with the values calculated from the pressure equation

$$z = 1 + (2\pi/3) \rho/kT \int_0^{\infty} \frac{du(r)}{dr} g(r) r^3 dr, \quad (1)$$

where $\rho = N/V$ is the number density, $u(r)$ the pair potential and $g(r)$ the radial distribution function. Eq. (1) is, as it is well-known, very sensitive to small inaccuracies of RDF. Even if a given theory fails in this test, it can still predict correctly the thermodynamic properties of system if we use for their determination the less sensitive energy equation

$$U/NkT = 2\pi\rho/kT \int_0^{\infty} u(r) g(r) r^2 dr, \quad (2)$$

where U is the configuration internal energy.

For testing in terms of Eqs (1) and (2), we chose the following approaches: Percus-Yevick (PY) and hypernetted chain (HNC) approximations, perturbation methods

by Andersen, Chandler and Weeks – high temperature approximation (HTA), optimized random phase approximation (ORPA) and exponential approximation (EXP), and perturbation methods combined with the Orstein–Zernike relation – the Lado method (LADO), called sometimes also the renormalized HNC, and the method by Madden and Fitts. We chose the most usual model of simple fluid, *i.e.* the Lennard–Jones potential

$$u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] \quad (3)$$

and the pair additivity rule. The computations were carried out for reduced densities $\bar{\rho} = N\sigma^3/V$ from 0 to 0.9 and reciprocal reduced temperatures $\beta = \varepsilon/kT$ from 0 to 1.3. The thermodynamic quantities z and U were calculated in the entire region with a step 0.05 for $\bar{\rho}$ and β . The complete tables of results are too extensive to be published and are available at authors on request. Only representative sample of results is given below.

Theories Tested

The Percus–Yevick method¹ is based on an approximation of direct correlation function, $c(r)$, by the relation

$$c(r) = \{\exp[-\beta u(r)] - 1\} y(r), \quad (4)$$

where

$$y(r) = \exp[\beta u(r)] g(r) \quad (5)$$

and on the Orstein–Zernike relation (OZ) between the direct and total correlation function $h(r) = g(r) - 1$

$$h(r) = c(r) + 2\pi\rho/r \int_0^\infty sh(s) \int_{|r-s|}^{r+s} tc(t) dt ds. \quad (6)$$

The HNC method² combines the OZ relation with the approximation

$$c(r) = \{\exp[-\beta u(r)] - 1\} y(r) + y(r) - 1 - \ln[y(r)]. \quad (7)$$

The simplest of the perturbation approaches developed by Andersen and coworkers is the high temperature approximation³. The reference potential, $u^0(r)$, to potential (1) is defined by the relation

$$u^0(r) = \begin{cases} u(r) + \varepsilon & r < \sqrt[6]{2} \\ 0 & r > \sqrt[6]{2}. \end{cases} \quad (8)$$

The perturbation component of the potential, $u^p(r)$, is given by the equation

$$u^p(r) = u(r) - u^o(r). \quad (9)$$

The radial distribution function is approximated by the same function for the reference system

$$g(r) = g^o(r) \quad (10)$$

and the RDF of reference system is determined in terms of the blip function approximation

$$y^o(r) = y_d^{\text{HS}}(r), \quad (11)$$

where y_d^{HS} is the y function of a system of hard spheres with diameter d . This diameter is obtained by solving the equation

$$\int_0^\infty y_d^{\text{HS}}(r) \{ \exp[-\beta u^o(r)] - \exp[-\beta u_d^{\text{HS}}(r)] \} r^2 dr = 0. \quad (12)$$

The more elaborated approaches of the above-mentioned authors, the ORPA⁴ and EXP⁵, were proposed for potentials with hard core. When applying them to the Lennard-Jones potential, the radial distribution function of trial potential is determined first

$$u^T(r) = \begin{cases} \infty & r < d \\ u^p(r) & r > d, \end{cases} \quad (13)$$

where u^p is defined by Eq. (9), and the conversion to potential (I) is carried out in terms of the blip function approximation

$$y(r) = y^T(r). \quad (14)$$

The radial distribution function of the trial system is in the ORPA given by the relation

$$g^T(r) = g_d^{\text{HS}}(r) + C(r) \quad (15)$$

and in the EXP approximation by

$$g^T(r) = g_d^{\text{HS}}(r) \exp[C(r)]. \quad (16)$$

The quantity $C(r)$ is a so-called renormalized potential⁵.

Lado⁶ stems from the general relation for the direct correlation function

$$c(r) = \{ \exp [-\beta u(r)] - 1 \} y(r) + y(r) - 1 - \ln [y(r)] + E(r), \quad (17)$$

where $E(r)$ is the sum of elementary diagrams. On subtracting the analogous equation for the reference system, we have

$$c(r) = c^\circ(r) + h(r) - h^\circ(r) - \ln [y(r)/y^\circ(r)] + E(r) - E^\circ(r). \quad (18)$$

In this relation, the approximation is then introduced

$$E(r) = E^\circ(r) \quad (19)$$

TABLE I

Thermodynamic functions at reduced density 0.100

β	Theory								
	MC	HNC	PY	HTA	MF1	ORPA	EXP	LADO	MF2
	Compressibility factor								
0.1	1.11	0.00	0.00	-0.01	-0.01	0.00	0.00	0.00	0.00
0.2	1.07	0.00	0.00	-0.03	-0.03	0.00	0.00	0.00	0.00
0.3	1.01	0.00	0.00	-0.04	-0.04	-0.01	0.00	0.00	0.00
0.4	0.95	0.00	0.00	-0.05	-0.05	-0.01	0.00	0.00	0.00
0.5	0.89	0.00	0.00	-0.06	-0.06	-0.02	0.00	0.00	0.00
0.6	0.82	0.00	0.00	-0.07	-0.07	-0.03	0.00	0.00	0.00
0.7	0.75	0.00	0.00	-0.08	-0.08	-0.04	0.00	0.00	0.00
0.8	0.67	0.00	0.00	-0.08	-0.08	-0.05	0.01	0.00	0.00
	Internal Energy								
0.1	-0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.2	-0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.3	-0.17	0.00	0.00	0.02	0.02	0.00	0.00	0.00	0.00
0.4	-0.25	0.00	0.00	0.03	0.03	0.00	0.00	0.00	0.00
0.5	-0.33	0.00	0.00	0.06	0.06	0.01	0.00	0.00	0.00
0.6	-0.43	0.00	0.00	0.09	0.02	0.02	0.00	0.00	0.00
0.7	-0.53	0.00	0.00	0.13	0.13	0.04	0.00	0.00	0.00
0.8	-0.65	0.00	0.00	0.20	0.20	0.07	0.01	0.00	0.00

and on inserting Eqs (18) and (19) into the OZ relation (6), the integral equation for the RDF is solved. In this work we have applied the Lado method to the trial potential (13). The RDF of the Lennard-Jones system was calculated in terms of Eq. (14).

Another combination of the perturbation approach with the OZ equation was proposed by Madden and Fitts⁷

$$g(r) = g^c(r) + g_{\text{HNC}}(r) - g_{\text{HNC}}^0(r). \quad (20)$$

The radial distribution function of reference system is determined in an analogous way

$$v^0(r) = v^{\text{HS}}(r) + v_{\text{PY}}^0(r) - v_{\text{PY}}^{\text{HS}}(r). \quad (21)$$

TABLE II

Thermodynamic functions at reduced temperature 2.740

\bar{v}	Theory								
	MC	HNC	PY	HTA	MFI	ORPA	EXP	LADO	MF2
	Compressibility factor								
0.1	0.97	0.00	0.00	-0.05	-0.05	-0.01	0.00	0.00	0.00
0.2	0.99	0.00	0.00	-0.08	-0.09	-0.03	0.00	-0.01	-0.01
0.3	1.06	0.02	0.01	-0.10	-0.11	-0.04	0.00	-0.02	-0.02
0.4	1.21	0.07	0.02	-0.09	-0.10	-0.04	0.00	-0.04	-0.03
0.5	0.48	0.16	0.04	-0.03	-0.06	-0.01	0.00	-0.03	-0.03
0.6	1.90	0.33	0.07	0.09	0.02	0.07	0.04	0.02	-0.01
0.7	2.57	0.60	0.08	0.26	0.13	0.21	0.10	0.11	0.04
0.8	3.60	0.94	0.01	0.46	0.23	0.38	0.18	0.25	0.07
0.9	5.15	1.32	-0.23	0.64	0.23	0.55	0.24	0.40	0.05
	Internal energy								
0.1	-0.22	0.00	0.00	0.02	0.02	0.01	0.00	0.00	0.00
0.2	-0.44	0.00	0.00	0.03	0.03	0.00	0.00	0.00	0.00
0.3	-0.65	0.00	0.00	0.03	0.03	0.00	0.00	0.00	0.00
0.4	-0.86	0.00	0.00	0.02	0.02	0.00	-0.01	0.00	-0.01
0.5	-1.07	0.02	0.00	0.02	0.02	0.00	-0.01	0.00	0.00
0.6	-1.26	0.04	0.00	0.02	0.02	0.00	-0.01	0.00	0.00
0.7	-1.43	0.08	0.00	0.04	0.03	0.02	0.00	0.00	0.00
0.8	-1.56	0.15	-0.01	0.06	0.04	0.05	0.02	0.03	0.00
0.9	-1.61	0.24	-0.05	0.09	0.05	0.08	0.04	0.05	0.00

The subscripts HNC and PY denote the functions obtained in terms of the HNC and PY approximations. Potential (8) was again chosen as the reference potential.

Eq. (21) is an alternative approach to the blip function approximation (11). By combining Eqs (10) and (21), we get a method analogous to the HTA. The given approach will be denoted by MF1 whereas the procedure employing Eqs (20) and (21) will be denoted by MF2.

A brief survey of methods used has been given in foregoing paragraph. Some technical and numerical details of their solutions are given in Appendix.

RESULTS AND DISCUSSION

In the region of low densities we can judge theories *a priori* according to their ability to describe lower virial coefficients. The PY and HNC yield exact second (B_2) and

TABLE III

Thermodynamic functions at reduced density 0.650

β	Theory								
	MC	HNC	PY	HTA	MF1	ORPA	EXP	LADO	MF2
Compressibility factor									
0.1	2.55	0.27	0.03	0.14	0.08	0.13	0.12	0.12	0.07
0.2	2.56	0.34	0.01	0.13	0.06	0.12	0.09	0.09	0.03
0.3	2.38	0.40	0.03	0.14	0.06	0.11	0.06	0.05	0.00
0.4	2.11	0.46	0.09	0.16	0.07	0.12	0.05	0.04	-0.01
0.5	1.76	0.54	0.18	0.19	0.10	0.15	0.05	0.03	0.00
0.6	1.38	0.61	0.29	0.23	0.13	0.17	0.04	0.03	0.01
0.7	0.98	0.67	0.40	0.25	0.15	0.18	0.03	-0.01	0.01
0.8	0.58	0.71	0.51	0.25	0.15	0.18	0.00	-0.04	-0.01
0.9	0.18	0.73	0.62	0.24	0.13	0.15	-0.06	-0.09	-0.04
Internal energy									
0.1	-0.07	-0.01	-0.06	-0.04	-0.05	-0.04	-0.04	-0.04	-0.05
0.2	-0.55	0.03	-0.02	0.00	0.00	0.00	-0.01	-0.01	-0.02
0.3	-1.04	0.06	0.00	0.03	0.02	0.01	0.00	0.01	0.00
0.4	-1.53	0.07	0.01	0.04	0.04	0.02	0.00	0.00	0.00
0.5	-2.02	0.07	0.01	0.05	0.05	0.02	-0.01	0.01	0.00
0.6	-2.52	0.07	0.02	0.06	0.06	0.03	-0.01	0.01	0.00
0.7	-3.02	0.07	0.02	0.07	0.07	0.03	-0.02	0.01	-0.01
0.8	-3.52	0.06	0.02	0.08	0.08	0.03	-0.04	0.00	-0.02
0.9	-4.03	0.06	0.03	0.10	0.10	0.03	-0.05	0.00	-0.03

third (B_3) virial coefficients. It is possible to show easily that the same holds for the MF2 and Lado methods. The exponential approximation leads only to the correct value of B_2 and the ORPA yields the correct value of B_2 in the limit $\beta \rightarrow 0$. The HTA and MF1 methods approximate the virial coefficients in terms of the reference system $B_2 = B_2^0$ and $B_3 = B_3^0$.

The compressibility factors obtained from the first five virial coefficients for the Lennard-Jones potential⁸ are compared in Table I with the results of theories tested at a reduced density equal 0.1. Here and in subsequent tables, the deviation of calculated value from "exact" data is always presented in the column of respective theory.

TABLE IV

Thermodynamic functions at reduced density 0.750

β	Theory								
	MC	HNC	PY	HTA	MF1	ORPA	EXP	LADO	MF2
Compressibility factor									
0.1	3.11	0.40	0.00	0.21	0.11	0.20	0.18	0.18	0.09
0.2	3.29	0.53	-0.04	0.24	0.10	0.21	0.14	0.15	0.05
0.3	3.20	0.64	-0.02	0.28	0.13	0.23	0.12	0.13	0.03
0.4	2.97	0.77	0.06	0.35	0.18	0.28	0.10	0.15	0.03
0.5	2.65	0.90	0.18	0.43	0.18	0.33	0.09	0.10	0.05
0.6	2.28	1.02	0.32	0.50	0.31	0.39	0.08	0.16	0.06
0.7	1.88	1.13	0.48	0.57	0.37	0.43	0.05	0.19	0.06
0.8	1.47	1.22	0.64	0.62	0.41	0.46	0.01	0.08	0.05
0.9	1.04	0.29	0.81	0.66	0.45	0.48	-0.04	0.08	0.04
1.0	0.58	1.37	1.01	0.71	0.49	0.51	-0.09	0.07	0.02
1.1	0.08	1.47	1.25	0.78	0.56	0.56	-0.12	0.05	0.04
Internal energy									
0.1	0.00	-0.03	-0.10	-0.06	-0.08	-0.07	-0.07	-0.07	-0.08
0.2	-0.56	0.05	-0.05	0.00	-0.02	-0.01	-0.02	-0.02	-0.03
0.3	-1.13	0.10	-0.02	0.03	0.02	0.02	0.00	0.01	-0.01
0.4	-1.71	0.13	0.01	0.06	0.05	0.04	0.02	0.02	0.01
0.5	-2.28	0.14	0.01	0.07	0.06	0.04	0.01	0.02	0.01
0.6	-2.86	0.15	0.03	0.08	0.07	0.05	0.01	0.02	0.00
0.7	-3.45	0.16	0.04	0.09	0.09	0.06	0.01	0.02	0.01
0.8	-4.04	0.17	0.06	0.10	0.10	0.06	0.00	0.02	0.00
0.9	-4.63	0.17	0.07	0.11	0.11	0.06	0.00	0.02	-0.01
1.0	-5.23	0.18	0.09	0.13	0.13	0.07	0.00	0.02	-0.01
1.1	-5.83	0.18	0.10	0.14	0.15	0.08	-0.01	0.01	-0.01

Further, the configuration internal energies are compared in Table I. The PY, HNC, LADO, and MF2 approaches are in perfect agreement with exact values. Likewise good results are yielded also by the EXP approximation, which gives evidence that the value of B_3 , and to a certain extent, B_4 , too, is close to the true value. As it can be expected, the results of HTA, ORPA and MF1 get worse with increasing β .

TABLE V

Thermodynamic functions at reduced density 0.850

β	Theory								
	MC	HNC	PY	HTA	MF1	ORPA	EXP	LADO	MF2
Compressibility Factor									
0.1	3.80	0.59	-0.04	0.34	0.17	0.33	0.29	0.30	0.15
0.2	4.26	0.78	-0.14	0.39	0.15	0.35	0.25	0.27	0.08
0.3	4.38	0.95	-0.16	0.45	0.17	0.38	0.19	0.21	0.03
0.4	4.31	1.14	-0.10	0.54	0.22	0.44	0.15	0.28	0.02
0.5	4.11	1.34	0.02	0.65	0.30	0.53	0.12	0.26	0.04
0.6	3.83	1.54	0.19	0.77	0.40	0.62	0.09	0.33	0.06
0.7	3.49	1.73	0.38	0.88	0.50	0.70	0.05	0.33	0.08
0.8	3.12	1.90	0.60	1.00	0.59	0.79	0.01	0.27	0.09
0.9	2.72	2.07	0.84	1.11	0.68	0.86	-0.05	0.21	0.10
1.0	2.29	2.22	1.11	1.21	0.77	0.94	-0.11	0.28	0.10
1.1	1.84	2.37	1.40	1.32	0.86	1.04	-0.17	0.35	0.11
1.2	1.37	2.52	1.72	1.43	0.96	1.09	-0.24	0.41	0.12
1.3	0.87	2.68	2.07	1.54	1.06	1.17	-0.29	0.07	0.13
Internal energy									
0.1	0.08	-0.01	-0.14	-0.07	-0.09	-0.07	-0.05	-0.04	-0.29
0.2	-0.54	0.10	-0.08	0.02	-0.01	0.01	-0.01	-0.01	-0.03
0.3	-1.17	0.16	-0.05	0.05	0.02	0.04	0.01	0.02	-0.01
0.4	-1.81	0.20	-0.03	0.07	0.04	0.06	0.02	0.03	0.00
0.5	-2.46	0.23	-0.02	0.09	0.06	0.06	0.02	0.03	0.00
0.6	-3.12	0.25	0.00	0.10	0.08	0.07	0.02	0.03	0.00
0.7	-3.78	0.27	0.02	0.11	0.09	0.08	0.02	0.02	0.00
0.8	-4.46	0.30	0.05	0.13	0.11	0.09	0.03	0.04	0.00
0.9	-5.13	0.31	0.07	0.13	0.12	0.09	0.03	0.03	-0.01
1.0	-5.81	0.32	0.10	0.14	0.14	0.10	0.04	0.02	-0.01
1.1	-6.50	0.35	0.13	0.16	0.16	0.11	0.06	0.03	-0.01
1.2	-7.19	0.36	0.17	0.18	0.18	0.13	0.07	0.02	-0.01
1.3	-7.88	0.38	0.20	0.19	0.19	0.14	0.09	0.07	-0.01

Behaviour of the theories at higher temperatures was tested along the traditional isotherm $kT/\epsilon = 2.74$. The smoothed Monte Carlo data⁹ are compared in Table II with the calculated values of z and U/NkT . The best results are yielded by the MF2. Surprisingly good is the PY approximation, whereas the HNC fails at higher densities. The EXP and LADO methods are very good as well, the former being somewhat better. The HTA and MF1 lead to analogous results at low densities, at higher densities MF1 is substantially better and comparable with EXP and LADO. The ORPA is only slightly better than the HTA. As it may be expected, the energy equation leads, for all the methods, to conspicuously better results than the pressure equation.

The region of dense gas and liquid was tested along the isochores $\tilde{\rho} = 0.65, 0.75$ and 0.85 . The results are presented in Tables III–VI. It follows from the comparison with the smoothed Monte Carlo data^{10–12} that the theories can be divided into

TABLE VI

Thermodynamic functions at reduced temperature 1.350

$\tilde{\rho}$	Theory								
	MC	HNC	PY	HTA	MF1	ORPA	EXP	LADO	MF2
Compressibility Factor									
0.1	0.72	0.00	0.00	-0.08	-0.08	-0.05	0.00	0.00	0.00
0.2	0.50	0.01	0.01	-0.17	-0.17	-0.10	0.01	-0.01	-0.01
0.3	0.35	0.05	0.05	-0.24	-0.24	-0.14	0.01	-0.03	-0.01
0.4	0.27	0.11	0.11	-0.24	-0.25	-0.14	-0.01	-0.07	-0.02
0.5	0.31	0.25	0.22	-0.12	-0.15	-0.08	-0.01	-0.09	-0.04
0.6	0.55	0.51	0.38	0.11	0.05	0.08	0.01	-0.05	-0.01
0.7	1.16	0.94	0.54	0.45	0.31	0.34	0.06	0.06	0.06
0.8	2.39	1.50	-0.09	0.80	0.51	0.62	0.07	0.21	0.11
0.9	4.63	2.07	0.23	0.97	0.42	0.77	-0.09	0.49	-0.06
Internal energy									
0.1	-0.58	0.00	0.00	0.16	0.16	0.05	0.01	0.00	0.00
0.2	-1.10	-0.05	-0.03	0.22	0.22	0.06	-0.01	-0.01	-0.03
0.3	-1.56	-0.08	-0.05	0.19	0.19	0.03	-0.05	-0.02	-0.05
0.4	-2.02	-0.05	-0.03	0.14	0.14	0.02	-0.06	-0.01	-0.02
0.5	-2.50	0.00	-0.01	0.10	0.10	0.03	-0.05	0.00	0.01
0.6	-2.98	0.04	0.01	0.08	0.08	0.02	-0.04	0.01	0.06
0.7	-3.47	0.12	0.04	0.09	0.09	0.05	0.00	0.02	0.16
0.8	-3.89	0.22	0.05	0.10	0.09	0.07	0.01	0.03	0.27
0.9	-4.19	0.35	0.01	0.13	0.10	0.09	0.03	0.04	0.37

three groups according to their success. The best ones are the MF2, EXP, LADO (in the given order), then the MF1, ORPA and HTA approaches, and the worst are the PY and HNC. A similar picture occurs with internal energy, but the differences are not so conspicuous.

The theories are compared on the critical isotherm of the Lennard-Jones fluid, $\beta = 1/1.35$. The agreement with the simulated data¹³ is here better than in the liquid region, the relative order of success of theories is similar. Only the PY approximation is here better than the HTA, MF1 and ORPA.

On the whole it is possible to say that the classical PY and HNC approximations describe well the structure only at low densities. Analogously to the hard sphere system, the Percus-Yevick method is better. Therefore it can be used to calculate thermodynamic quantities in terms of the energy function as it has been stated before by Barker and Henderson¹⁴.

The HTA approximation is popular with regard to its numerical unpretentiousness. However, it is not suitable for describing structure. The values of internal energy are not as well too good even at high temperatures. Similar case occurs when calculating thermodynamic functions in terms of the perturbation expression for the Helmholtz energy¹⁵. The main reason of failure is apparently the blip function approximation for the MF1 yields at higher densities substantially better results.

The ORPA method is likewise demanding as the substantially better EXP approximation. Therefore the ORPA does not seem to be significant for simple fluids.

The MF2, LADO and EXP methods proved to be most successful. From the three approaches mentioned, the most accurate is the Madden-Fitts method. At the same time it is, however, the most time-consuming. Three integral equations are namely solved in it. The exponential approximation is numerically least laborious and at the same time rather better than the Lado method. We assume that this method is the most suitable one for simple fluids.

APPENDIX

In this Appendix, the most important numerical details of solution of the methods tested are summarized.

The methods based on solution of integral equations (PY, HNC, MF1, MF2) were solved by direct iteration¹⁶. The Simpson rule with interval $\Delta r = 0.04\sigma$ and maximum distance $r_{\max} = 8\sigma$ was used for the integration. The iterations were finished at the maximum relative error in function $y(r)$ lower than 0.0001. The maximum error of the compressibility factors is lower than 0.005 and for the reduced internal energy is lower than 0.002. (An exception is only an immediate vicinity of the critical point, where the error may be as much as several times higher.)

To solve all the perturbation theories, first it is necessary to define density of the hard sphere reference system. Through all the work, the uniform way was used of choosing the hard sphere diameter in terms of the blip function approximation (12). The properties of the hard sphere system were then calculated by means of the recently reported¹⁷ parametrization of Monte Carlo data.

The ORPA and EXP methods were adapted for solution by introducing the function

$$H(r) = C(r) + u^p(r)/kT. \quad (22)$$

Eqs (15) and (16) can then be rewritten easily into the forms

$$y^T(r) = [y_d^{HS}(r) + H(r) - u^p(r)/kT] \exp [u^p(r)/kT], \quad (23)$$

or

$$y^T(r) = y_d^{HS}(r) \exp [H(r)], \quad (24)$$

respectively. These equations are, owing to the continuity of functions $y(r)$ and $H(r)$, substantially numerically more advantageous. Besides, the problems with extrapolating the function $y^T(r)$ for $r < d$ do not take place.

To solve the iteration Lado method, which is really too much time-consuming, a new numerical procedure was elaborated. Its detailed description can be found elsewhere¹⁸.

The HTA, ORPA, EXP and Lado methods require the numerical three-dimensional Fourier transformation. The reversible Lado procedure¹⁹ with the parameters $\Delta r = 0.02\sigma$ and $r_{\max} = 6\sigma$ was employed. The iterations were finished for mean relative error in $y(r)$ lower than 0.0005. The uncertainty of results obtained grew with the complexity of method used. Whereas the maximum error of the HTA was lower than 0.005 and 0.001 for z and U/NkT , respectively, for the Lado method reached up to 0.03 and 0.05, respectively. The errors mentioned are, however, attained only for the highest densities and very low temperatures. In most calculations, however, they are substantially lower. The numerical inaccuracy of results is therefore considerably lower than the errors of individual theories and uncertainty of Monte Carlo data and is sufficient for testing the theories.

REFERENCES

1. Percus J. K., Yevick G. L.: *Phys. Rev.* **110**, 1 (1958).
2. Van Leeuwen J. M. J., Groeveld J., De Boer J.: *Physica (Utrecht)* **25**, 792 (1959).
3. Weeks J. D., Chandler D., Andersen H. C.: *J. Chem. Phys.* **54**, 5237 (1971).
4. Andersen H. C., Chandler D., Weeks J. D.: *J. Chem. Phys.* **56**, 3812 (1972).
5. Andersen H. C., Chandler D., Weeks J. D.: *J. Chem. Phys.* **57**, 1918 (1972).
6. Lado F.: *Phys. Rev. A* **8**, 2548 (1973).
7. Madden W. G., Fitts D. D.: *Chem. Phys. Lett.* **28**, 427 (1974); *Mol. Phys.* **28**, 1095 (1975).
8. Barker J. A., Leonard P. J., Pompe A.: *J. Chem. Phys.* **41**, 4206 (1966).
9. Hansen J. P.: *Phys. Rev. A* **2**, 221 (1970).
10. Levesque D., Verlet L.: *Phys. Rev.* **182**, 307 (1969).
11. Verlet L.: *Phys. Rev.* **159**, 98 (1968).
12. Hansen J. P., Verlet L.: *Phys. Rev.* **183**, 151 (1969).
13. Levesque D., Viellard-Baron J.: *Physica (Utrecht)* **36**, 254 (1967).
14. Barker J. A., Henderson D., Watts R. O.: *Phys. Lett.* **31 A**, 48 (1970).
15. Labík S.: *Thesis*. Prague Institute of Chemical Technology, Prague 1979.
16. Broyles A. A.: *J. Chem. Phys.* **33**, 456 (1960).
17. Labík S., Malijevský A.: *Mol. Phys.* **42**, 739 (1981).
18. Lado F.: *J. Comp. Phys.* **8**, 417 (1971).
19. Labík S., Malijevský A.: *This Journal*, in press.

Translated by J. Linek.