

Thermodynamic perturbation theory for the (12-6- n) fluids

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Abstract. A perturbation method in which attractive forces are taken as perturbation of the repulsive (reference) forces is applied to calculate the thermodynamic properties of (12-6- n) fluids in terms of the properties of hard-sphere fluid. The numerical values of the thermodynamic properties (free energy per particle, compressibility and excess internal energy) for a range of temperature and density are given for (12-6-8) fluids. Further, two perturbation schemes are adopted to evaluate the total radial distribution function using the EXP version of the optimized cluster theory (OCT). The numerical results are reliable as reported at two states ($T^*=1.036$, $\rho^*=0.65$ and $T^*=0.719$, $\rho^*=0.85$) for the (12-6-8) fluid and the Lennard-Jones (12-6) fluid as well.

Keywords. Equilibrium structure of simple liquids; radial distribution function; optimized cluster theory; Pade' approximants; high temperature approximation.

1. Introduction

The aim of the present work is to study the thermodynamic properties of fluids consisting of molecules interacting with (12-6- n) potential using the perturbation theory (PT) developed by Weeks, Chandler and Andersen (WCA) (1971) and Verlet and Weis (VW) (1972). The original formulation of perturbation theory by Zwanzig (1955) is applicable only to molecules with hard core. The theory has been further extended and applied to other systems by many workers (Barker and Henderson 1967; Mansoori and Canfield 1968; Rasaiah and Stell 1970; Chandler and Weeks 1970). In these theories the pair potential is written as the sum of two parts—a reference (positive) part and a perturbation (negative) part.

Weeks *et al* (1971) studied the equilibrium structure of simple liquids by using a new perturbation scheme for separating the intermolecular potential. In this scheme the reference system is characterized by that part of the potential which gives rise to the repulsive force and vanishes when the force vanishes. The remaining part of the potential which leads to the attractive force is treated as a perturbation on the reference potential. Verlet and Weis (1972) have examined in detail the conceptual advantages of various approximations of WCA theory and presented an analytic form of it. For a Lennard-Jones (12-6) fluid they have shown that the WCA separation of the potential into reference and perturbation leads to a rapid convergence of the perturbation series at liquid densities. Using the same separation scheme we have recently developed (Shukla *et al* 1976; 1978) a thermodynamic perturbation theory for the equilibrium—properties of fluids of non-spherical molecules in the presence of three-body forces. Using the VW version of WCA theory we calculate in this paper the thermodynamic properties of (12-6- n) fluid.

The pair potential model which we use in this calculation is written as

$$U(r) = 4 \epsilon [(\sigma/r)^{12} - (\sigma/r)^6 + A (\sigma/r)^n] \quad (1)$$

where r is the intermolecular separation, A an arbitrary constant and ϵ and σ are, respectively, the potential well depth and molecular diameter if $A \rightarrow 0$. The integer n can have any value between 1 and ∞ . Equation (1) represents the Lennard-Jones (12-6) model with an added interaction term which varies with r^{-n} .

Following WCA, we write

$$U(r) = U_0(r) + \lambda w(r), \quad 0 \leq \lambda \leq 1 \quad (2)$$

where $U_0(r)$ is the reference system pair potential and $w(r)$ the perturbation potential. $U_0(r)$ includes all the repulsive forces of the pair potential and $w(r)$ all the attractive forces.

$$\begin{aligned} U_0(r) &= U(r) + \epsilon_m(n, A), \quad r \leq r_m \\ &= 0, \quad \text{otherwise} \\ \lambda w(r) &= -\epsilon_m(n, A), \quad r \leq r_m \\ &= U(r), \quad \text{otherwise} \end{aligned} \quad (3)$$

here r_m is the separation at which the potential energy is minimum and ϵ_m is the depth of the potential at $r = r_m$.

In the following sections, the free energy per particle, compressibility and excess internal energy for (12-6- n) fluids are calculated. Also a reference potential is defined and the reference radial distribution function (RDF) is calculated. The total RDF is calculated using the exponential version of the optimized cluster theory (EXP OCT) (Andersen and Chandler 1972).

2. Calculations and results

2.1. Free energy per particle

Verlet and Weis (1972) have shown that in the calculation of free energy of fluids good results are obtained even if one evaluates only the zero and first-order terms of the perturbation series and neglects other terms. The total free energy per particle of the system can be written as

$$\beta \hat{f} = \beta \hat{f}_0 + \frac{1}{2} \rho \beta \int w(r) \hat{g}_0(r) d\bar{r} \quad (4)$$

where $\beta = 1/kT$, ρ is the number density of molecules, \hat{f}_0 the free energy per particle of the reference system i.e. of the system of particles interacting through $U_0(r)$ and

$\hat{g}_0(r)$ the reference system pair correlation function. The reference system free energy is given as

$$\beta \hat{f}_0 = \beta f_{\text{HS}}^{\text{ex}} + 4 \beta \delta \Delta f \quad (5)$$

where

$$\beta f_{\text{HS}}^{\text{ex}} = \frac{4 - 3\eta}{(1 - \eta)^2} \times \eta \quad (6)$$

is the excess free energy of the hardsphere system and

$$\beta \Delta f = \frac{3\eta^2 (1 + 1.759\eta - 5.249\eta^3)}{(1 - \eta)^3} \quad (7)$$

with

$$\eta = \frac{1}{6} \pi \rho^* C^3$$

$$C = \frac{d}{\sigma}; \quad \rho^* = \rho d^3 \quad (8)$$

d is the diameter of a hardsphere, the value of which is determined by the expression (WCA 1971)

$$d = d_B [1 + (\sigma_{11}/2 \sigma_{00}) \delta] \quad (9)$$

where d_B and δ are the temperature dependent simple integrals

$$d_B = \int_0^{\infty} [1 - \exp(-\beta U_0(r))] dr$$

$$\delta = \int_0^{\infty} \left(\frac{r}{d_B} - 1\right)^2 \frac{d}{dr} [\exp(-\beta U_0(r))] dr \quad (10)$$

and σ_{00} is the value of RDF at the core and σ_{11} is determined in terms of RDF and its first derivative at the core;

$$\sigma_{00} = (1 - \frac{1}{2} \eta) / (1 - \eta)^3$$

$$\sigma_{11} = \frac{(2 - 7.5 \eta + \frac{1}{2} \eta^2 - 5.785 \eta^3 - 1.51 \eta^4)}{(1 - \eta)^4} \quad (11)$$

For the potential model of eq. (1) we evaluate the hardsphere diameter of a fluid for several values of A ($= \pm 0.60, \pm 0.40, \pm 0.20, \pm 0.10$) and n ($= 6, 8, 10, 12, 18$)

at many temperatures and densities. In fact d is determined through a self-consistency criterion i.e. we use d_B as a trial value and eventually iterate through the above equations to obtain an accurate value of d . d values are listed in table 1 for $n = 8$ and T^* (kT/ϵ) = 0.75, 1.15, 1.35 and 2.74. At these reduced temperatures the computer simulation (Levesque and Verlet 1969) and other results, for $L-J$ (12-6) potential are available. It can be seen from table 1 that the value of hardsphere diameter decreases with the increase of temperature as well as density.

The first order contribution to the free energy $\beta \tilde{f}_1$, is given as (Verlet and Weis 1972)

$$\begin{aligned} \beta \tilde{f}_1 &= \frac{1}{2} \rho \beta \int w(r) \tilde{g}_0(r) d\bar{r} \\ &= 48 \eta_w \beta \left[\frac{I_{12}^{\text{HS}} - I_{12}^2}{d_w^{12}} - \frac{I_6^{\text{HS}} - I_6^2}{d_w^6} - \frac{I_0^2}{4} \right] \\ &\quad + 48 \eta_w \beta \left[A \frac{I_n^{\text{HS}} - I_n^2}{d_w^n} - (\epsilon_m - I) \frac{I_0^2}{4} \right] \end{aligned} \quad (12)$$

where

$$\eta_w = \eta - \eta^2 / 16 \quad (13.1)$$

$$d_w = d (\eta_w / \eta)^{1/3} \quad (13.2)$$

$$\begin{aligned} I_n^2 &= \int_1^{r_m/d_w} x^2 \frac{Y_w(x, \eta_w)}{x^n} dx, \quad x = r/\sigma \\ I_n^2 &= \frac{\alpha_0}{n-2} + \frac{\alpha_1}{(n-2)(n-3)} + \frac{\alpha_2}{(n-2)(n-3)(n-4)} \\ &\quad - \left(\frac{d_w}{r_m}\right)^n \left[\frac{\alpha_0 - \alpha_1 + \alpha_2/2}{n-2} \left(\frac{r_m}{d_w}\right)^2 + \frac{\alpha_1 - \alpha_2}{n-3} \times \left(\frac{r_m}{d_w}\right)^3 + \frac{\alpha_2/2}{n-4} \left(\frac{r_m}{d_w}\right)^4 \right]. \end{aligned} \quad (13.3)$$

Here

$$\alpha_0 = (1 + \eta_w/2) / (1 - \eta_w)^3$$

$$\alpha_1 = (1 - 5 \eta_w - 5 \eta_w^2) / (1 - \eta_w)^3$$

$$\alpha_2 = -3 \eta_w (2 - 4 \eta_w - 7 \eta_w^2) / (1 - \eta_w)^4$$

and

$$I_n^{\text{HS}} = \int_1^{\infty} dx x^2 \frac{y_w(x, \eta_w)}{x^n} \quad (13.4)$$

$y_w(x, \eta_w)$ is the hardsphere radial distribution function for the reference system. The I_n^{HS} integral is evaluated by replacing the reference $\tilde{g}_0(r)$ by the pair correlation function of hardsphere, of effective diameter d . For $n=6, 8, 10, 12$ and 18 I_n^{HS} has been calculated by Stell *et al* (1974). Their results are given in Pade' approximants which are superior to that of the virial approximation results (Kozac and Rice 1968). These results are quoted as

$$I_6^{\text{HS}} = \frac{1}{3} + \frac{(0.225099 X + 0.057361 X^2)}{(1.0 - 0.040323 X)} \quad (13.5)$$

$$I_8^{\text{HS}} = \frac{1}{5} + \frac{(0.173442 X + 0.039956 X^2)}{(1.0 - 0.249462 X)} \quad (13.6)$$

$$I_{10}^{\text{HS}} = \frac{1}{7} + \frac{(0.139665 X + 0.030805 X^2)}{(1.0 - 0.374023 X)} \quad (13.7)$$

$$I_{12}^{\text{HS}} = \frac{1}{9} + \frac{(0.116298 X)}{(1.0 - 0.671067 X + 0.144763 X^2)} \quad (13.8)$$

$$I_{18}^{\text{HS}} = \frac{1}{15} + \frac{0.076670 X}{(1.0 - 0.803539 X + 0.144763 X^2)} \quad (13.9)$$

with $X = \rho^* d^{*3}$.

The reference and first-order contributions to Helmholtz free energy per particle have been evaluated for $A = \pm 0.60, \pm 0.40, \pm 0.20, \pm 0.10$ and $n = 6, 8, 10, 12, 18$ at many temperatures and densities. These contributions corresponding to $n = 8$ are given in table 2 at $T^* = 0.75, 1.35$ and 2.74 . It can be seen from the table that both the parts of free energy contribute significantly throughout the temperature and density range of our investigation. While the first order contribution is much large as compared to reference contribution, they are of opposite sign, resulting in mutual cancellation and negative value for free energy.

2.2. Compressibility and internal energy

The total compressibility of the system can be written as

$$\hat{Z}_T = \hat{Z}_0 + \hat{Z}_1 \quad (14)$$

where \hat{Z}_0 is the compressibility of the reference system and \hat{Z}_1 is the first order contribution to the compressibility.

The reference system compressibility is given (VW 1972) as

$$\hat{Z}_0 = Z_{\text{HS}}(\eta) + 4\eta\delta \left(\frac{1}{2} \tau_2 - \tau_1 \sigma_{11} / 2 \sigma_{00} \right) \quad (15)$$

where

$$Z_{\text{HS}}(\eta) = (1 + \eta + \eta^2 - \eta^3) / (1 - \eta)^3 \quad (16)$$

Table 1. Hard-sphere diameter for (12-6-8) fluid.

T^*	ρ^*	A	-0.60	-0.40	-0.20	-0.10	0.00	0.10	0.20	0.40	0.60
0.75	0.10	0.9608	0.9814	1.0037	1.0152	1.0269	1.0391	1.0516	1.0774	1.1042	
	0.50	0.9602	0.9807	1.0026	1.0139	1.0255	1.0374	1.0495	1.0743	1.0996	
	0.65	0.9600	0.9802	1.0019	1.0130	1.0245	1.0361	1.0479	1.0717	1.0957	
	0.85	0.9594	0.9793	1.0003	1.0111	1.0221	1.0332	1.0442	1.0658	1.0863	
1.15	0.10	0.9503	0.9696	0.9902	1.0009	1.0119	1.0232	1.0347	1.0583	1.0826	
	0.50	0.9497	0.9687	0.9890	0.9995	1.0102	1.0212	1.0323	1.0549	1.0779	
	0.65	0.9493	0.9682	0.9882	0.9985	1.0091	1.0197	1.0305	1.0523	1.0742	
	0.85	0.9485	0.9670	0.9866	0.9965	1.0066	1.0166	1.0266	1.0464	1.0655	
1.35	0.10	0.9461	0.9649	0.9848	0.9952	1.0059	1.0169	1.0280	1.0507	1.0743	
	0.50	0.9454	0.9639	0.9836	0.9937	1.0042	1.0147	1.0255	1.0473	1.0695	
	0.65	0.9449	0.9633	0.9827	0.9927	1.0029	1.0132	1.0236	1.0447	1.0657	
	0.85	0.9441	0.9621	0.9810	0.9907	1.0003	1.0099	1.0196	1.0389	1.0572	
2.74	0.10	0.9249	0.9414	1.0152	0.9679	0.9770	0.9863	0.9958	1.0154	1.0351	
	0.50	0.9240	0.9403	0.9574	0.9661	0.9749	0.9839	0.9930	1.0116	1.0301	
	0.65	0.9235	0.9395	0.9564	0.9649	0.9736	0.9823	0.9912	1.0089	1.0265	
	0.85	0.9225	0.9382	0.9544	0.9626	0.9709	0.9792	0.9875	1.0035	1.0192	

Table 2. Free energy per particle for (12-6-8) fluids.

A	ρ^*	T^*	0.75		1.35		2.74			
			βf_0	$-\beta f_1$	βf_0	$-\beta f_1$	βf_0	$-\beta f_1$		
-0.60	0.10	0.10	0.1973	1.2923	0.1878	0.7314	0.5436	0.1748	0.3695	0.1947
	0.50	0.50	1.3005	7.8049	1.2194	4.3608	3.1414	1.1117	2.1644	1.0527
	0.65	0.65	1.9133	10.7697	1.7791	5.9902	4.2111	1.3046	2.9553	1.3507
	0.85	0.85	3.0191	15.0777	2.7664	8.3398	5.5734	2.4499	4.0849	1.6351

0.40	0.10	0.2111	1.1040	0.8929	0.1999	0.6249	0.4249	0.1949	0.3156	0.1307
	0.50	1.4218	6.6756	5.2538	1.3223	3.7243	2.4021	1.1937	1.8448	0.6511
	0.65	2.1156	9.1934	7.0777	1.9475	5.1037	3.1562	1.7356	2.5119	0.7764
	0.85	3.4030	12.8045	9.4014	3.0752	7.0668	3.9916	2.6804	3.4528	0.7723
0.20	0.10	0.2268	0.9391	0.7122	0.2135	0.5317	0.3182	0.1962	0.2684	0.0722
	0.50	1.5665	5.6772	4.1107	1.4415	3.1619	1.7204	1.2870	1.5628	0.2757
	0.65	2.3618	7.7941	4.4322	2.1462	4.3176	2.1713	1.8864	2.1197	0.2333
	0.85	3.8837	10.7737	6.8899	3.4497	5.9334	2.4837	2.9493	2.8923	0.0569
0.10	0.10	0.2353	0.8651	0.6297	0.2208	0.4898	0.2689	0.2021	0.2472	0.0451
	0.50	1.6472	5.2240	3.5768	1.5079	2.9066	1.3989	1.3373	1.4348	0.0975
	0.65	2.5017	7.1558	4.6541	2.2582	3.9595	1.7013	1.9685	1.9414	0.0271
	0.85	4.1645	9.8419	5.6775	3.6638	5.4153	1.7514	3.0981	2.6373	0.4608
0.00	0.10	0.2443	0.7964	0.5521	0.2285	0.4508	0.2223	0.2082	0.2274	0.0193
	0.50	1.7347	4.8003	3.0636	1.5744	2.6680	1.0887	1.3905	1.3155	0.0750
	0.65	2.6554	6.5576	3.9022	2.3797	3.6243	1.2446	2.0561	1.7749	0.2812
	0.85	4.4790	8.9660	4.4870	3.8979	4.9294	1.0314	3.2585	2.3991	0.8594
0.10	0.10	0.2537	0.7328	0.4791	0.2366	0.4147	0.1780	0.2145	0.2091	0.0054
	0.50	1.8296	4.4080	2.5754	1.6560	2.4456	0.7896	1.4469	1.2043	0.2426
	0.65	2.8244	5.9979	3.1735	2.5111	3.3112	0.8001	2.1496	1.6197	0.5297
	0.85	4.8310	8.1444	3.3134	4.1529	4.4751	0.3222	3.4309	2.1773	1.2536
0.20	0.10	0.2637	0.6740	0.4102	0.2451	0.3813	0.1361	0.2213	0.1922	0.0291
	0.50	1.9329	4.0370	2.1041	1.7379	2.2388	0.5009	1.5071	1.1011	0.4059
	0.65	3.0104	5.4756	2.4652	2.6528	3.0196	0.3668	2.2497	1.4756	0.7741
	0.85	5.2229	7.3759	2.1529	4.4307	4.0522	-0.3786	3.6153	1.9715	1.6438
0.40	0.10	0.2855	0.5699	0.2844	0.2631	0.3222	0.0591	0.2356	0.1621	0.0735
	0.50	2.1672	3.3788	1.2116	1.9185	1.8696	-0.0489	1.6384	0.9175	0.7209
	0.65	3.4387	4.5382	1.0995	2.9708	2.4984	-0.4724	2.4691	1.2191	1.2500
	0.85	6.1293	5.9961	-0.1331	5.0649	3.2990	-1.7659	4.0166	1.6068	2.4098
0.60	0.10	0.3094	0.4825	0.1731	0.2829	0.2725	-0.0104	0.2507	0.1369	0.1138
	0.50	2.4419	2.8179	0.3760	2.1264	1.5563	-0.5701	1.7822	0.7624	1.0198
	0.65	3.7384	3.7384	-0.2143	3.3413	2.0566	-1.2847	2.7129	1.0030	1.7099
	0.85	7.2217	4.8287	-2.3930	5.7968	2.6668	-3.1300	4.4663	1.3025	3.1637

Table 3. Compressibility and the total internal energy for (12-6-8) fluids.

A	ρ^*	T^*	0.75			1.35			2.74		
			Z^o	Z^T	$-UT$	Z^o	Z^T	$-UT$	Z^o	Z^T	$-UT$
-0.60	0.10	1.2094	0.9389	1.1988	0.4283	0.9319	1.1843	0.7968	0.9229		
	0.50	2.8091	5.7093	2.6659	5.6459	2.4825	5.4581	-0.1068	5.4581		
	0.65	3.9947	7.9131	3.7128	7.7747	3.3639	7.4321	-0.2723	7.4321		
	0.85	6.6236	11.1064	5.9491	10.8011	5.1639	10.1430	0.0495	10.1430		
-0.40	0.10	1.2249	0.7899	1.2123	0.5531	0.7883	1.1955	0.8642	0.7746		
	0.50	3.0264	4.8601	2.8444	4.7647	2.6187	4.5371	0.4214	4.5371		
	0.65	4.4264	6.7131	4.0562	6.5255	3.6158	6.1213	0.5530	6.1213		
	0.85	7.6539	9.3290	6.7248	8.9416	5.6977	8.1791	1.4532	8.1791		
-0.20	0.10	1.2428	0.6668	1.2276	0.6658	0.6623	1.2080	0.9260	0.6401		
	0.50	3.2948	4.0965	3.0581	3.9712	2.7772	3.6818	0.9276	3.6818		
	0.65	4.9737	5.6227	4.4783	5.3854	3.9128	4.8869	1.3591	4.8869		
	0.85	8.9968	7.6782	7.7085	7.2031	6.3303	6.2914	2.8554	6.2914		
-0.10	0.10	1.2525	0.3338	1.2359	0.7181	0.6056	1.2146	0.9549	0.0781		
	0.50	3.4491	2.9347	3.1797	-0.3142	3.6057	2.8644	1.1741	3.2775		
	0.65	5.2966	5.1139	4.7219	-0.1124	4.8527	4.0789	1.7592	4.2954		
	0.85	9.8109	6.8917	8.2801	1.7677	6.3684	6.6899	3.5677	5.3706		
0.00	0.10	1.2627	0.4162	1.2446	0.7678	0.5523	1.2215	0.9824	0.5208		
	0.50	3.6200	3.4417	3.3124	0.1204	3.2564	2.9580	1.4172	2.2895		
	0.65	5.6606	4.2224	4.9899	0.6050	4.3389	4.2891	2.1586	3.7316		
	0.85	10.7438	6.0556	9.9044	3.0847	4.5496	7.0928	4.2896	4.4804		
0.10	0.10	1.2736	0.4939	1.2539	0.8149	0.5019	1.2287	1.0088	0.4677		
	0.50	3.8095	3.0971	3.4570	0.5476	2.9213	3.0586	1.6571	2.5364		
	0.65	6.0707	4.1627	5.2842	1.3202	3.8408	4.4540	2.5579	3.1971		
	0.85	11.7997	2.3422	8.2416	3.3269	4.5788	6.5796	4.2247	3.5879		
0.20	0.10	1.2852	0.5674	1.2636	0.8597	0.4546	1.2363	1.0342	0.4182		
	0.50	4.0197	2.7989	3.6142	0.9693	2.5993	3.1667	1.8946	2.1962		
	0.65	6.5305	3.7146	5.6071	2.0368	3.3572	2.9565	2.9565	2.6852		
	0.85	12.9639	4.6519	0.3162	5.7370	3.9608	7.9523	5.7398	2.7874		

0.40	0.10	1.3106	-0.7025	10.3879	1.2844	0.9427	0.3697	1.2526	1.0820	0.3259
	0.50	4.5093	0.5184	2.2427	3.9712	1.8024	1.9973	3.4055	2.3631	1.5371
	0.65	7.6087	2.3303	2.8583	6.3526	3.4883	2.4343	5.1238	3.7498	1.6772
	0.85	15.4434	-9.1366	3.1561	11.9661	8.4308	2.4358	8.8679	7.1317	1.1268
0.60	0.10	1.3388	0.8232	0.3185	1.3074	1.0182	0.2977	1.2699	1.1258	0.2400
	0.50	5.1072	1.8545	1.7301	4.3929	2.6275	1.4496	3.6745	2.8268	0.8796
	0.65	8.9286	4.7524	2.0507	7.2260	4.9495	1.5559	5.6462	4.5509	0.6513
	0.85	17.8101	13.1102	1.8482	13.5708	10.8564	0.0072	9.8444	8.4940	-0.5065

is the compressibility of hardsphere system, and τ_1 and τ_2 are obtained in terms of RDF at the core;

$$\begin{aligned}\tau_1 &= 2 \sigma_{00} + a_1 - A_p \\ \tau_2 &= 2 \sigma_{00} + 4 a_1 + a_2 - 4 A_p\end{aligned}\quad (17)$$

with

$$A_p = \frac{27}{2} \left[\frac{\eta_w^3}{(1 - \eta_w)^6} \right] \frac{(1 - 0.7117 \eta_w - 0.114 \eta_w^2)^2}{(1 + \frac{1}{2} \eta_w)}.$$

For the first order contribution to the compressibility, we obtain:

$$\hat{Z}_1 = \frac{1}{1 - 3L} \left[\eta_w \frac{\partial \beta \hat{f}_1}{\partial \eta_w} - 3L \cdot \xi_2 \right] \quad (18)$$

where

$$\begin{aligned}L &= \frac{\eta_w}{d_w} \frac{\partial d_w}{\partial \eta_w} = \lambda_w - \frac{1}{48} \eta \left(1 - \frac{\eta}{8}\right)^{-1} \\ \xi_2 &= 16 \eta_w \beta \left[12. \frac{I_{12}^{\text{HS}} - I_{12}^2}{d_w^{12}} - 6. \frac{I_6^{\text{HS}} - I_6^2}{d_w^6} + An \frac{I_n^{\text{HS}} - I_n^2}{d_w^n} \right]\end{aligned}$$

with

$$\lambda_w = \eta_w \frac{\partial}{\partial \eta_w} \left(\frac{\sigma_{11}}{2 \sigma_{00}} \right) \delta.$$

For evaluating the total excess internal energy we use the relation (VW 1972)

$$\hat{U}_T = \hat{f}_1 + 4 \delta' \Delta f + 3 (\hat{Z}_T - 1 - \xi_2) (d'_B/d_B + \delta' (\sigma_{11} | 2 \sigma_{00})) \quad (19)$$

where d'_B and δ' are, respectively, the temperature derivative of d_B and δ .

For a (12-6-8) fluid the calculated values of compressibility and internal energy are given in table 3 at $T^* = 0.75, 1.35$ and 2.74 .

2.3. The reference system radial distribution function

We adopt two different approaches to define the reference potential and study the reference system properties in terms of the properties of hardsphere fluid. The first approach is the same as given by eq. (3). The RDF of this reference system is given by

$$g_{\text{ref}}(r) = \exp \left[-\beta U_{\text{ref}}^{(12-6-n)}(r) \right] y_0(r, d) \quad (20)$$

where $y_0(r, d)$ is the function of a reference system of hard sphere of diameter d which represents the cluster integral with the reference pair potential only.

In the second method we take the L-J potential to be the reference and the rest of our (12-6- n) pair potential to be the perturbation. That is

$$U^{(12-6-n)}(r) = U_{L-J}^{(12-6)}(r) + 4\epsilon A (\sigma/r)^n$$

where

$$U_{L-J}^{(12-6)}(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6]. \quad (21)$$

Following WCA, we get

$$\begin{aligned} U_{L-J}^{(12-6)}(r) &= U_{L-J}^{\text{ref}}(r) + \epsilon_m, & r \leq 2^{1/6} = r_m \\ &= 0, & \text{otherwise} \\ \lambda w(r) &= -\epsilon_m, & r \leq 2^{1/6} = r_m \\ &= U_{L-J}^{(12-6)}(r), & \text{otherwise} \end{aligned}$$

and determine d by the scheme presented in eq. (9) and the reference RDF by eq. (20). The hard sphere diameters for the U_{L-J}^{ref} and $U_{(12-6-8)}^{\text{ref}}$ are 1.01295 and 0.99169 respectively at the reduced temperature $T^* = 1.036$ and the reduced number density $\rho^* (= \rho\sigma^3) = 0.65$. Similarly at $T^* = 0.719$ and $\rho^* = 0.85$ the hard sphere diameters for the above two reference potentials are 1.02360 and 1.00165 respectively.

2.4. The total RDF

The high temperature approximation (HTA) (Andersen *et al* 1972) of the RDF of the actual system is

$$[g(r)]_{\text{HTA}} = g_{\text{ref}}(r). \quad (23)$$

The calculations of Andersen *et al* (1972), Andersen and Chandler (1972), Wang *et al* (1973) and Sung and Chandler (1974) show that at high densities (23) affords a reasonably accurate theory of Lennard-Jones (12-6) liquids. At low densities, however, the structure is no longer dominated entirely by the repulsive forces and the attraction must be accounted for. They have used the optimized cluster theory (OCT) to obtain correction to the HTA for the L-J (12-6) fluid and are able to account for most of the small errors in the HTA and if the EXP version of OCT is used to compute the correction to the HTA, excellent results are obtained for the RDF. For this sake we adopt the EXP version of the OCT of Andersen and Chandler (1972) in which the total RDF is written as

$$g_{\text{T}}(R) = g_{\text{ref}}(R) \exp [C(R)] \quad (24)$$

where $C(R)$ is the renormalized potential. The expression for this in the Fourier transform for the (12-6- n) pair potential is given as

$$\rho^{*2} C(R) = \frac{1}{2\pi^2 R} \int_0^\infty (k\sigma) \sin(k\sigma R) \left[\frac{F_d^2(k\sigma) \phi_p^{(12-6-n)}(k\sigma)}{1 - F_d(k\sigma) \phi_p^{(12-6-n)}(k\sigma)} \right] d(k\sigma) \quad (25)$$

where

$$F_d(k\sigma) = \frac{\rho^*}{1 - \rho^* C_d(k\sigma)} \quad (26)$$

$$\begin{aligned} \phi_p^{\text{Total}}(k\sigma) &= \frac{4\pi}{T^*(k\sigma)^2} [-R_m \cos(R_m k\sigma) + \sin(R_m k\sigma)] / (k\sigma) \\ &\quad - \frac{4\pi}{T^*(k\sigma)^2} \int_{R_m}^\infty R U_{(R)}^{*\text{Total}} \sin(k\sigma R) dR. \end{aligned} \quad (27)$$

Here R_m values are known for our pair potential and the second integral will be determined by the Gaussian quadrature method.

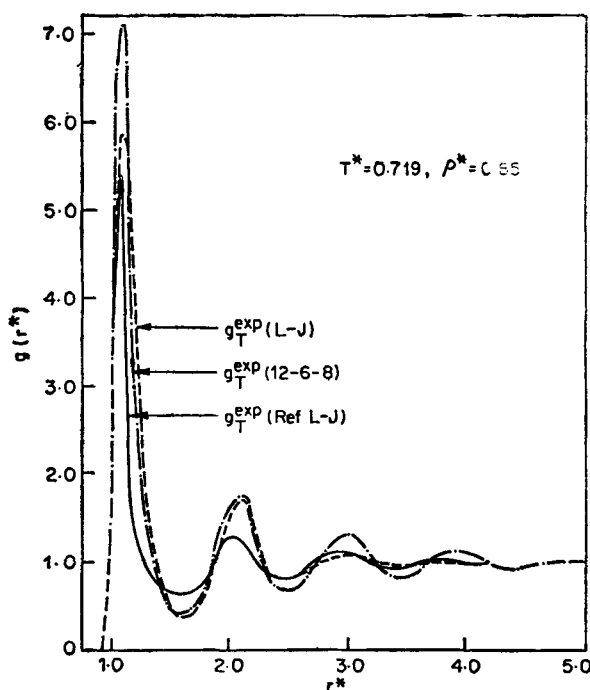
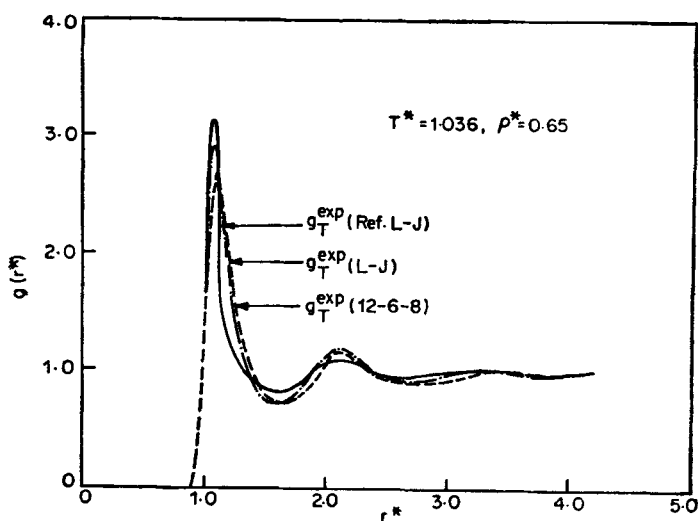
$$\begin{aligned} C_d(k\sigma) &= -\frac{4\pi\lambda_1}{(k\sigma)^2} [-d^* \cos(k\sigma d^*) + \sin(k\sigma d^*)] / (k\sigma) \\ &\quad - \frac{24\pi \eta_w \lambda_2}{d^* (k\sigma)^2} \left[-d^{*2} \cos(k\sigma d^*) + 2d^* \frac{\sin(k\sigma d^*)}{(k\sigma)} \right. \\ &\quad \left. + \frac{2 \cos(k\sigma d^*)}{(k\sigma)^2} - \frac{2}{(k\sigma)^2} \right] - \frac{2\pi \eta_w \lambda_1}{(k\sigma)^2 d^{*3}} \left[-d^{*4} \cos(k\sigma d^*) \right. \\ &\quad \left. + \frac{4d^{*3} \sin(k\sigma d^*)}{(k\sigma)} + \frac{12d^{*2} \cos(k\sigma d^*)}{(k\sigma)^2} - \frac{24d^* \sin(k\sigma d^*)}{(k\sigma)^3} \right. \\ &\quad \left. - \frac{24 \cos(k\sigma d^*)}{(k\sigma)^4} + \frac{24}{(k\sigma)^4} \right]. \end{aligned} \quad (28)$$

In the above expressions the notations have the following meanings:

$$\begin{aligned} R &= \frac{r}{\sigma}; R_m = \frac{r_m}{\sigma}; U^{*\text{Total}} = \frac{U^{\text{Total}}}{\epsilon} \\ \eta_w &= \eta - \eta^2/16; \lambda_1 = (1 + 2\eta_w)^2 / (1 - \eta_w)^4; \\ \lambda_2 &= -(1 + \frac{1}{2} \eta_w)^2 / (1 - \eta_w)^4 \end{aligned} \quad (29)$$

ϕ_p is the perturbation potential.

The total RDF obtained from eq. (24) for the (12-6-8) as well as for the L-J (12-6) perturbation potentials are given in figures 1 and 2 at states $T^* = 1.036$, $\rho^* = 0.65$ and $T^* = 0.719$, $\rho^* = 0.85$, respectively. As seen from the figures when the potential is perturbed according to WCA criterion (eq. 3) we find that at lower density and higher temperature the first peak of the total RDF g_T^{EXP} lies in between the $T(12-6-8)$



Figures 1 and 2. Comparative study of the total RDFs; Lennard-Jones.

total RDF for the L-J g_{L-J}^{EXP} and the RDF for (12-6-8) $g_{(12-6-8)}^{\text{EXP}}$ when the reference is L-J and exceeds at higher density and lower temperature. Thus, we find that, on the average, the effect of the additional potential on the RDF is very well accounted for.

3. Conclusions

We have shown that the idea of relating the hardsphere fluid model to more realistic potential models can be used to calculate the thermodynamic properties and the pair correlation function of (12-6- n) fluids provided the hardsphere diameter is chosen properly. A correct knowledge of the hardsphere system is an essential requirement of this kind of theory. Therefore, the tabulated values of the thermodynamic properties, the radial distribution functions as well as of temperature dependent hardsphere diameters, are of much use for those engaged in this area of investigation. Further, to study the properties of such a model fluid is in itself of much interest.

For the (12-6- n) potential model at present, since no simulation values of the thermodynamic properties as well as RDF are available, our results cannot be compared and tested directly. However, similar calculations for the (12-6) potential agree well with the simulation results (Andersen and Chandler 1972; Barker and Henderson 1972, 1976; Ram and Singh 1977). This fact together with the good agreement of the PTRDF and simulation result leads us to believe that our results are reliable. In conclusion, we wish to emphasise that the VW version of WCA perturbation theory, the use of which reduces to a great extent the computational labour involved in evaluating the properties of dense fluids, is quite useful and simple for the study of thermodynamic properties of fluids. Also, the features of wide applicability and simplicity of the EXP version of OCT have motivated us to employ this method to study the simple dense fluids of the (12-6- n) pair potential model.

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