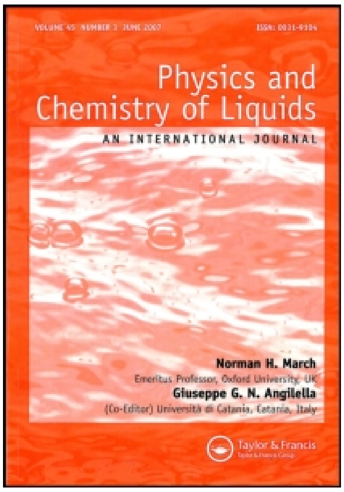

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Integral Equations and the Optimised Cluster Theory for Triangular Well Potential

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Of the various integral equations that have been derived to calculate the radial distribution function of classical fluids the Percus–Yerick (PY), Hypernetted chain equation (HNC) and the Mean spherical model (MSM) have been considered. The structure and thermodynamic properties were calculated for triangular well potential and the results are compared with the Monte Carlo simulation results. Also results for thermodynamic properties using the optimised cluster theory (OCT) of Andersen *et al.* were presented.

INTRODUCTION

In this paper we study the applicability of current liquid state theories for the case of the triangular well fluid (TW), in which molecules interact with the pair potential

$$u(r) = \begin{cases} \infty, r < \sigma \\ \dfrac{n\varepsilon}{(n-1)}\left(\dfrac{r}{n\sigma} - 1\right), \sigma < r < n\sigma \\ 0, r > n\sigma \end{cases} \tag{1}$$

and we consider the case $n = 2$ throughout since the Monte Carlo simulation results are available for such a case. Though triangular well fluid is a model fluid, it is particularly appropriate as a testing ground for theories because it seems to amplify differences in various theories much more than for other models. Also for appropriately chosen parameters the TW fluid gives qualitative agreement with the properties of real simple fluids such as argon. The TW fluid is also of some interest because of the greater statistical accuracy which can be expected for data resulting from numerical integrations.[2] Ausloos *et al.*[3] recently applied the Zwanzig's perturbation theory[4] for triangular well fluid. Smith *et al.*[5] have generated semi-exact results for thermodynamic properties for the triangular well fluid using Barker-Henderson perturbation theory[6] and Tago[7] reported the fourth virial coefficients for TW fluid.

INTEGRAL EQUATIONS

The direct correlation function $c(r)$ is defined by the Ornstein–Zernike (OZ) relation

$$h(r_{12}) = c(r_{12}) + \rho \int h(r_{13})c(r_{23})\mathrm{d}\mathbf{r}_3 \tag{2}$$

Here $\rho(=N/V)$ is the number density, $h(r)$ is the total correlation function defined in terms of the radial distribution function $g(r)$ by

$$h(r) = g(r) - 1 \tag{3}$$

The OZ equation is a definition of $c(r)$ which must be supplemented if an equation which can be solved is to be obtained. The percus–Yevick (PY) approximation[8] supplements the closure approximation

$$c(r) = f(r)y(r) \tag{4}$$

where

$$f(r) = e^{-\beta u(r)} - 1 \tag{5}$$

$$y(r) = g(r)\exp[\beta u(r)] \tag{6}$$

$\beta = 1/k_B T$, T is the temperature and k_B is the Boltzmann constant.

The hypernetted chain (HNC) approximation[9–11] relating $c(r)$ and $g(r)$ is given by

$$c(r) = f(r)y(r) + y(r) - 1 - \ln y(r) \tag{7}$$

The mean spherical model (MSM)[12] is based on the assumption

$$\begin{aligned} c(r) &= f(r)y(r), \qquad r < \sigma \\ &= -\beta u(r), \qquad r > \sigma \end{aligned} \tag{8}$$

where σ is such that $u(\sigma) = 0$ and $u(r) > 0$ for $r < \sigma$. The MSM and PY approximations are identical for the hard sphere system (i.e. when $\beta = 0$).

Recently, Anderson and Chandler[13] proposed an approximation known as the optimised cluster theory of liquids. The Mayer cluster series for the

Helmholtz free energy and the pair correlations functions are transformed using topological reductions suggested by Morita and Hiroike[14] to more compact forms involving a renormalised potential. In this application the potential is divided into

$$u(r) = u_0(r) + u_1(r) \tag{9}$$

where $u_0(r)$ is the reference part of the potential given by

$$u_0(r) = \infty,\ r < \sigma \tag{10}$$

$$0,\ r > \sigma$$

and $u_1(r)$ is the attractive perturbation. Defining

$$\phi(r) = -\beta u_1(r) \tag{11}$$

and its Fourier transform

$$\hat{\phi}(k) = \int \mathrm{d}\mathbf{r} \exp(-i\mathbf{k}\cdot\mathbf{r})\phi(r) \tag{12}$$

the renormalised potential $c_L(r)$ is given by

$$\rho^2 c_L(r) = \frac{1}{(2\pi)^3}\int \mathrm{d}\mathbf{k} \exp(i\mathbf{k}\cdot\mathbf{r})\frac{\hat{F}_0^2(k)\hat{\phi}(k)}{(1-\hat{F}_0(k)\hat{\phi}(k))} \tag{13}$$

where the hypervertex $F_0(\mathbf{r}_1, \mathbf{r}_2)$ is defined by

$$F_0(\mathbf{r}_1, \mathbf{r}_2) = \rho\delta(\mathbf{r}_1, \mathbf{r}_2) + \rho^2 h_0(\mathbf{r}_1, \mathbf{r}_2) \tag{14}$$

Here $\delta(\mathbf{r}_1, \mathbf{r}_2)$ is the Dirac delta function and $h_0(\mathbf{r}_1, \mathbf{r}_2)$ is the total correlation function for the reference system. Anderson *et al.* proposed the linearised exponential approximation for the radial distribution function given by

$$g(r) = g_0(r)[1 + c_L(r)] \tag{15}$$

and the exponential approximation (EXP) given by

$$g(r) = g_0(r)e^{c_L(r)} \tag{16}$$

where $g_0(r)$ is the r.d.f. for the reference system.

THERMODYNAMIC PROPERTIES

Once the RDF is obtained, thermodynamic properties can be obtained from the energy equation

$$\frac{U}{Nk_BT} = \frac{3}{2} + \frac{2\pi\rho}{k_BT}\int r^2 u(r) g(r)\mathrm{d}r \tag{17}$$

and from the pressure equation

$$\frac{PV}{Nk_BT} = 1 - \frac{2\pi\rho}{3k_BT}\int r^3 \frac{\mathrm{d}u}{\mathrm{d}r} g(r)\mathrm{d}r \tag{18}$$

and the compressibility equation

$$\beta\left(\frac{\partial P}{\partial \rho}\right)_T = 1 - 4\pi\rho \int c(r)r^2 \, \mathrm{d}r \tag{19}$$

An exact RDF will lead to consistent results for the thermodynamics properties as calculated from the pressure, energy and the compressibility equations of state and an approximate RDF destroy the self consistency.

CALCULATIONS INTEGRAL EQUATIONS

The PY, HNC and MSM integral equations were written in the r-space by writing the volume integral in the OZ equation in terms of bipolar coordinates and the resulting equation is solved by an iterative technique using a grid size of 0.05σ. Convergence was enhanced by using Broyle's mixing parameter using the formula

$$Y_{\text{in}}^{(n+1)} = (1 - \alpha)Y_{\text{out}}^{(n)} + \alpha Y_{\text{out}}^{(i-1)} \tag{20}$$

where Y_{in}^{n} and Y_{out}^{n} are the nth input and output and α is the mixing parameter. The iterations were terminated when

$$|Y^{n+1} - Y^{n}| \leq 0.001$$

the resulting $g(r)$ and $c(r)$ were used in the pressure, energy and compressibility equation and all the integrals were programmed using Simpsons rule.

CALCULATIONS FOR OCT

Since the properties of the fluid of molecules interacting through the potential (9) must be independent of the value of the perturbation $u_1(r)$ for the physically impossible interparticle separations $r < \sigma$, it is equally clear that the LEXP for the free energy and the pair distribution function depend on the value of the perturbation inside the hard core, since the renormalized potential is a functional of $\phi(r)$. This unphysical behaviour was eliminated by choosing $u_1(r)$ in such a way that

$$c_L(r) = 0, r < \sigma \tag{21}$$

This implies that

$$\frac{\delta V a_{\mathrm{ring}}}{\delta \phi(r)} = \frac{1}{2} \rho^2 c_L(r) = 0 \tag{22}$$

where a_{ring} is the ring contributions to the free energy and is given by

$$a_{\mathrm{ring}} = \frac{-1}{2(2\pi)^3} \int \mathrm{d}\mathbf{k} \{\hat{F}_0(k)\hat{\phi}(k) + \ln[1 - \hat{F}_0(k)\hat{\phi}(k)]\} \tag{23}$$

In order to solve the variational problem given by Eq. (22) we assumed a trial solution of the form

$$\begin{aligned} \phi(r) &= \sum_{n=0}^{3} a_n \left(1 - \frac{r}{\sigma}\right)^n, \quad r < \sigma \\ &= \hat{\phi}(r), \qquad\qquad r > \sigma \end{aligned} \tag{24}$$

and minimised Va_{ring} with respect to the coefficients a_0, a_1, a_2, a_3 by Newton–Raphson method. The hard sphere radial distribution functions were calculated from the PY theory using Verlet–Weis method.[15]

The radial distribution functions obtained from the PY, HNC and MSM theories are compared in Figures 1–4, with the Monte Carlo results. In Figures 5 and 6 the direct correlation functions were plotted. In Table I

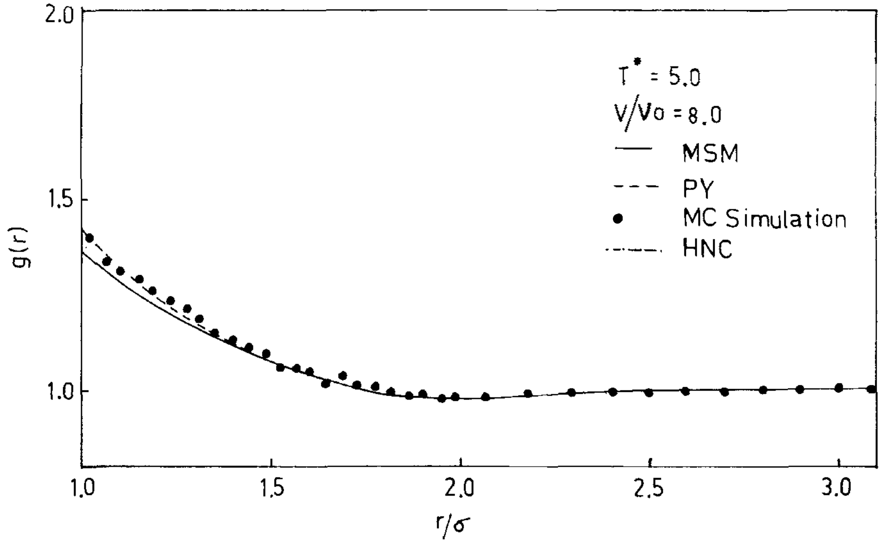

FIGURE 1 Radial distribution function for the TW fluid at T* = 5.0 and $v/v_0 = 8.0$ ($V_0 = N\sigma^3/\sqrt{2}$).

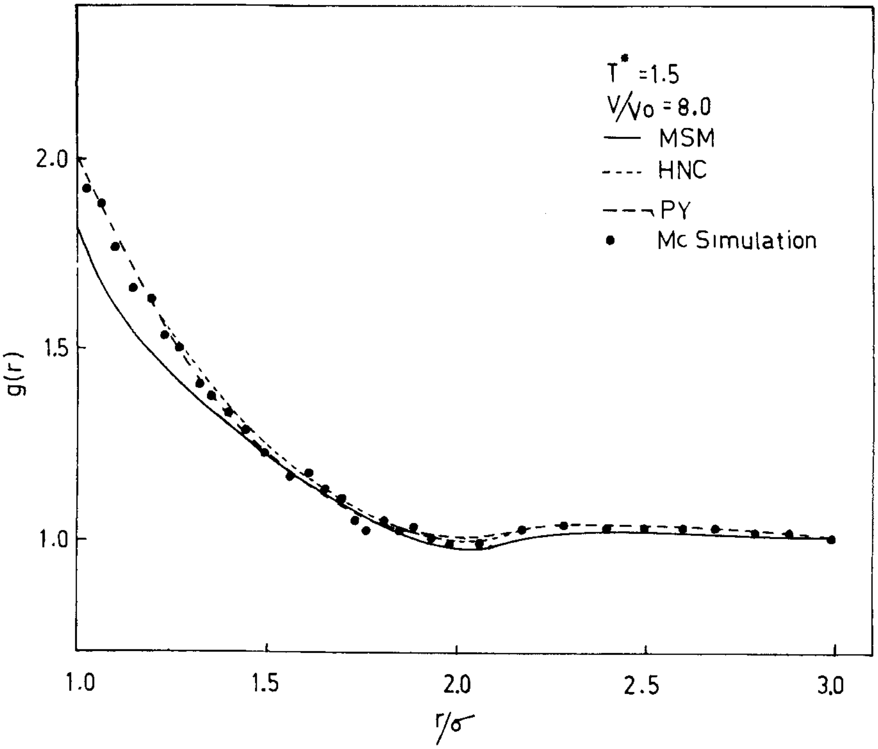

FIGURE 2 Same as Figure 1 but for $T^* = 1.5$ and $v/v_0 = 8.0$.

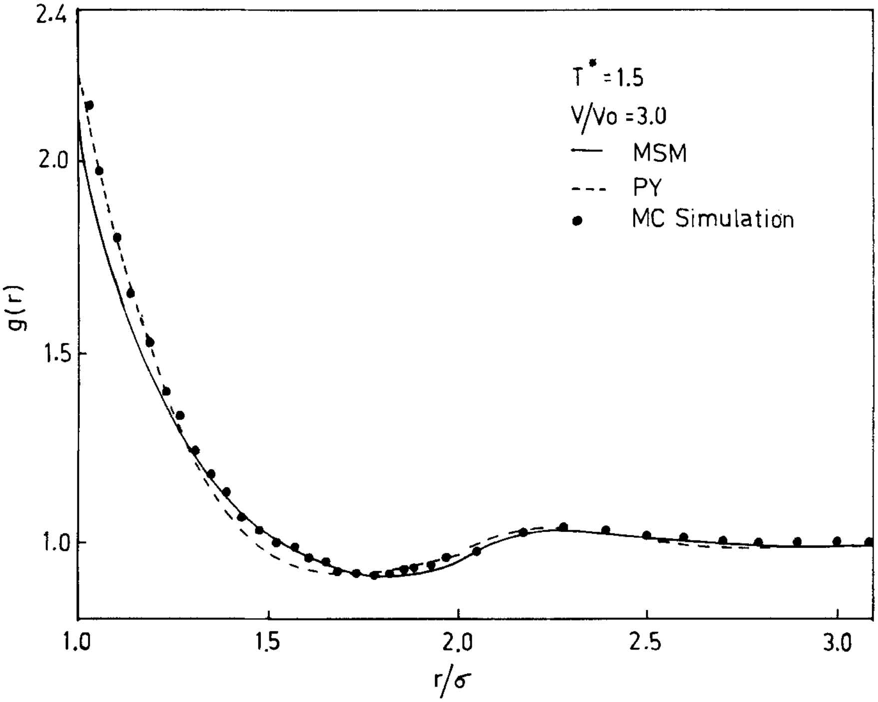

FIGURE 3 Same as Figure 1 but for $T^* = 1.5$ and $v/v_0 = 3.0$.

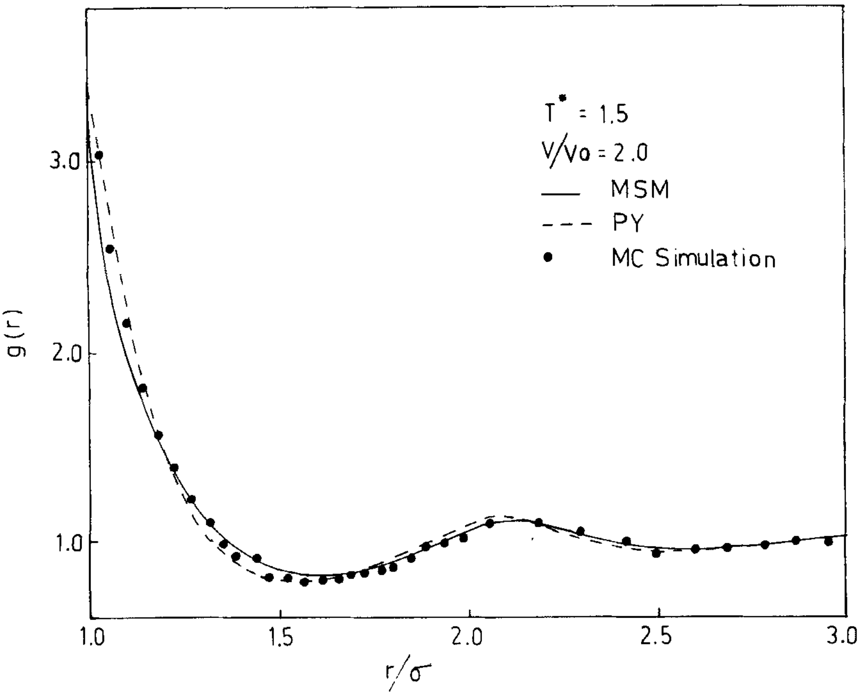

FIGURE 4 Same as Figure 1 but for $T^* = 1.5$ and $v/v_0 = 2.0$.

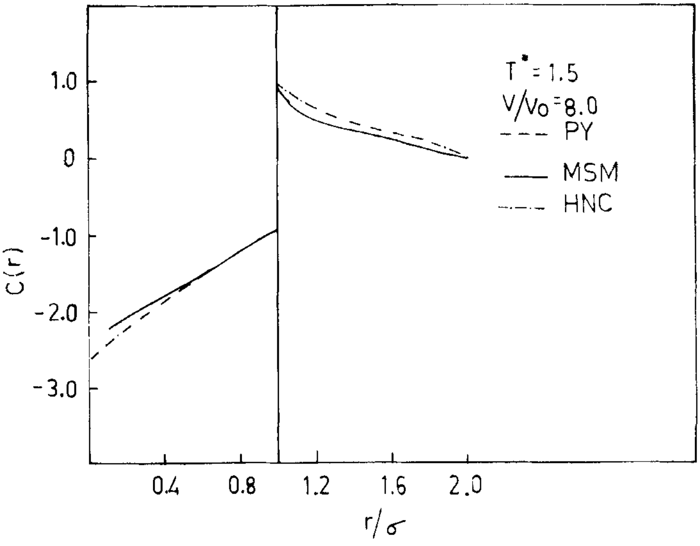

FIGURE 5 Direct correlation function for the TW fluid at $T^* = 1.5$ and $v/v_0 = 8.0$.

TABLE I

Thermodynamic properties from the integral equations

		PV/Nk_BT				U/Nk_BT				$\beta(\partial P/\partial\rho)T$		
V/V_0	T^*	MSM	PY	HNC	MC	MSM	PY	HNC	MC	MSM	PY	HNC
8.0	5.0	1.214	1.232	1.232	1.234	−0.230	−0.232	−0.240	−0.234	1.504	1.557	1.548
8.0	1.5	0.603	0.643	0.639	0.650	−0.890	−0.931	−0.922	−0.935	0.527	0.440	0.421
3.0	1.5	0.603	0.654	—	0.638	−2.194	−2.234	—	−2.263	1.641	1.604	—
2.0	1.5	2.180	2.232	—	2.232	−3.262	−3.331	—	−3.413	8.921	7.797	—
1.75	1.5	3.432	—	—	3.712	−3.707	—	—	−3.928	16.466	—	—
1.75	0.8	−0.374	—	—	0.020	−6.915	—	—	−7.375	8.135	—	—

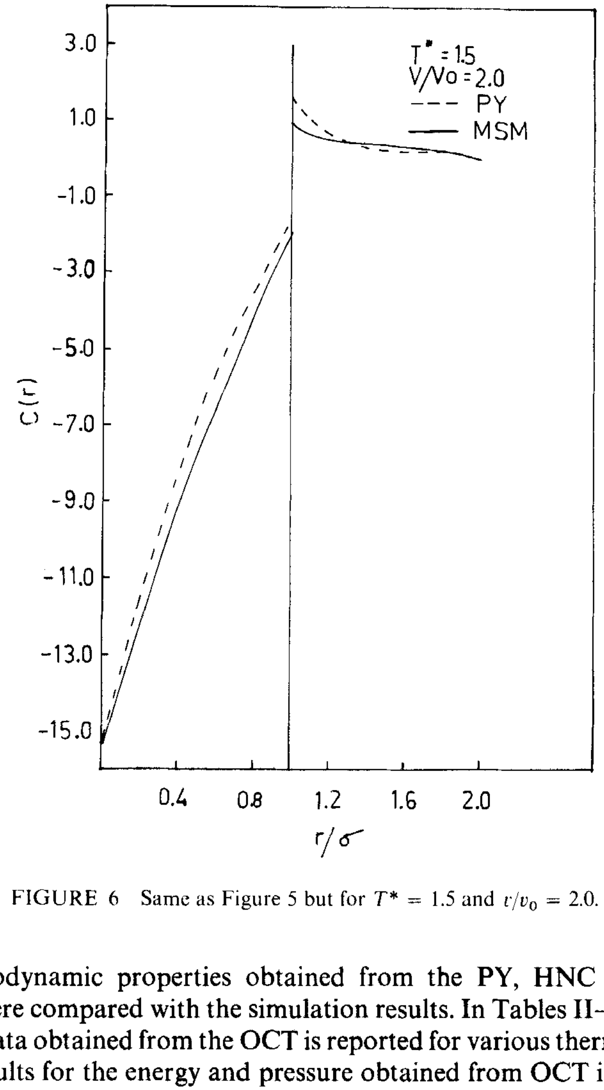

FIGURE 6 Same as Figure 5 but for $T^* = 1.5$ and $v/v_0 = 2.0$.

the thermodynamic properties obtained from the PY, HNC and MSM theories were compared with the simulation results. In Tables II–IV thermodynamic data obtained from the OCT is reported for various thermodynamic states. Results for the energy and pressure obtained from OCT is compared with simulation results in Figures 7–9.

A comparison of Figures 1–4 reveals that the MSM $g(r)$ is too low near the contact. This feature of MSM has been observed for other hard core fluids like the square well fluid by Tago and Swamy.[16] The PY and HNC results compare well with the simulation results. The MSM and PY pressures calculated from the pressure Eq. (17) are not so good. It is sensitive to the error of $g(r)$ at the hard core. The energy is not due to the details of $g(r)$ in contrast with the pressure. The PY energy is better than the MSM energy. The

TABLE II

OCT values of U/Nk_BT obtained from the energy equation

$\beta\varepsilon$ / $\rho\sigma^3$	0.1	0.2	0.3	0.4	0.5	0.55	0.6	0.65	0.7	0.75	0.8	0.85	0.9
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1	−0.0629	−0.1300	−0.2010	−0.2283	−0.3527	−0.3897	−0.4283	−0.4668	−0.5051	−0.5433	−0.5814	−0.6193	−0.6574
0.2	−0.1306	−0.2664	−0.4078	−0.5544	−0.7052	−0.7815	−0.8580	−0.9346	−1.0111	−1.0873	−1.1633	−1.2394	−1.3157
0.3	−0.2034	−0.4100	−0.6213	−0.8388	−1.0623	−1.1756	−1.2895	−1.4037	−1.5179	−1.6319	−1.7459	−1.8601	−1.9747
0.4	−0.2809	−0.5623	−0.8433	−1.1294	−1.4231	−1.5724	−1.7229	−1.9900	−2.0256	−2.1773	−2.3292	−2.4815	−2.6347
0.5	−0.3669	−0.7248	−1.0750	−1.3646	−1.7885	−1.9726	−2.1586	−2.3461	−2.5345	−2.7236	−2.9132	−3.1037	−3.2955
0.6	−0.4588	−0.9001	−1.3215	−1.7360	−2.1596	−2.3768	−2.5971	−2.8200	−3.0447	−3.2707	−3.4980	−3.7266	−3.9571
0.7	−0.5586	−1.0547	−1.5859	−2.0580	−2.5382	−2.7861	−3.0390	−3.2961	−3.5563	−3.8189	−4.0836	−4.3504	−4.6197
0.8	−0.6674	−1.3044	−1.8779	−2.3999	−2.9268	−3.202	−3.4851	−3.7749	−4.0697	−4.3683	−4.6701	−4.9750	−5.2833
0.9	−0.7865	−1.5495	−2.2260	−2.7759	−3.3299	−3.6268	−3.9367	−4.2569	−4.5851	−4.9190	−5.2577	−5.6006	−5.9478
1.0	−0.9175	−1.8677	−2.413	—	−3.7561	−4.0648	−4.3954	−4.7431	−5.1029	−5.4713	−5.8463	−6.2271	−6.6133
1.1	−1.0628	—	−2.6102	—	−4.2356	−4.5228	−4.8645	−5.2347	−5.6237	−6.0254	−6.4372	−6.8547	−7.2798
1.2	−1.2259	—	−3.0864	—	−4.5974	−5.0243	−5.3492	−5.7335	−6.1482	−6.5815	−7.0275	−7.4833	−7.9475
1.3	−1.4130	−2.2235	—	−5.1131	−5.2251	−5.3153	−5.8615	−6.2431	−6.6775	−7.1402	−7.6203	−8.1132	−8.6162

TABLE III

OCT values of $P/\rho k_B T$ obtained from the pressure equation

$\frac{\beta\varepsilon}{\rho\sigma^3}$	0.1	0.2	0.3	0.4	0.5	0.55	0.6	0.65	0.7	0.75	0.8	0.85	0.9
0.0	1.2393	1.5500	1.9588	2.4808	3.1732	3.5993	4.0912	4.6608	5.3229	6.0953	7.0007	8.0671	9.3304
0.1	1.1662	1.4014	1.7330	2.2028	2.8544	3.2963	3.8094	4.4233	5.1598	6.0467	7.1199	8.4255	10.025
0.2	1.0898	1.2472	1.4995	1.8870	2.4711	2.8618	3.3364	3.9123	4.6111	5.4600	6.4940	7.7587	9.3140
0.3	1.0102	1.0898	1.2639	1.5724	2.0764	2.4279	2.8640	3.4020	4.0630	4.8737	5.8686	7.0923	8.6036
0.4	0.9321	0.9284	1.0263	1.2570	1.6822	1.9948	2.3925	2.7766	3.5156	4.2882	5.2438	6.4263	7.8936
0.5	0.8387	0.7615	0.7855	0.9726	1.2887	1.5624	1.9216	2.3836	2.9688	3.7032	4.6194	5.7607	7.1838
0.6	0.7456	0.5873	0.5399	0.6242	0.8959	1.1309	1.4517	1.8755	2.4228	3.1188	3.9956	5.0955	6.4743
0.7	0.6464	0.4162	0.2863	2.3055	0.5039	0.7005	0.9828	1.3683	1.8775	2.5350	3.3723	4.4306	5.7651
0.8	0.5399	0.2025	0.0181	−0.0174	0.1131	0.2715	0.5150	0.8621	1.3330	1.9519	2.7495	3.7662	5.0562
0.9	0.4247	−0.0228	−0.2860	−0.3526	−0.2763	−0.1555	0.0489	0.3570	0.7898	1.3694	2.1271	3.1021	4.3474
1.0	0.2989	−0.3100	−0.5350	—	−0.6660	−0.5793	−0.4148	−0.1464	0.2467	0.7875	1.5054	2.4384	3.6391
1.1	0.1599	—	−0.7373	—	−1.0711	−0.9998	−0.8746	−0.6479	−0.2948	0.2066	0.8843	1.7753	2.9310
1.2	0.0037	—	−1.0973	—	−1.4158	−1.4264	−1.3280	−1.1460	−0.8348	−0.3734	0.2634	1.1124	2.2231
1.3	−0.1764	−0.6680	−3.2285	−2.2033	−1.8724	−1.7555	−1.7766	−1.6378	−1.3724	−0.9525	−0.3566	0.4499	1.5154

TABLE IV

OCT values of $\beta(\partial P/\partial\rho)_T$ obtained from the compressibility equation

$\frac{\beta\varepsilon}{\rho\sigma^3}$	0.1	0.2	0.3	0.4	0.5	0.55	0.6	0.65	0.70	0.75	0.80	0.85	0.9
0.0	1.5133	2.2768	3.4210	5.1541	7.8171	9.6632	11.9836	14.9172	18.6502	23.4345	29.6149	37.6695	48.2696
0.1	1.3926	2.0354	3.0621	4.6817	7.2215	8.9997	11.2907	14.169	17.8460	22.5736	28.6963	36.6921	47.2325
0.2	1.2684	1.7904	2.7004	4.2073	6.6497	8.3353	10.5971	13.4202	17.0414	21.7123	27.7773	35.7143	46.1951
0.3	1.1399	1.5405	2.3349	3.7303	6.0637	7.6695	9.9024	12.6706	16.2361	20.8505	26.8579	34.7363	45.1576
0.4	1.0078	1.2844	1.9644	3.2500	5.4757	7.0025	9.2066	11.9202	15.4303	19.9883	25.9382	33.758	44.1198
0.5	0.8652	1.0196	1.587	2.7653	4.8854	6.3334	8.5096	11.1690	14.6238	19.1255	25.0181	32.7794	43.0817
0.6	0.7160	0.7427	1.1996	2.2746	4.2918	5.6615	7.8111	10.4166	13.8166	18.2623	24.0976	31.8005	42.0434
0.7	0.5405	0.4478	0.7969	1.7764	3.6941	4.9860	7.1106	9.6629	13.0085	17.3984	23.1766	30.8212	41.0048
0.8	0.3818	0.1246	0.3674	1.2615	3.0904	4.3051	6.4079	8.9078	12.1995	16.5339	22.2552	29.8416	39.966
0.9	0.1891	−0.2503	−0.1280	0.7216	2.4778	3.6157	5.7021	8.1509	11.3893	15.6686	21.3333	28.8617	38.9250
1.0	−0.0282	−0.7788	−0.4422	—	1.8505	2.9123	4.9921	7.3917	10.5777	14.8025	20.4108	27.8813	37.8874
1.1	−0.2808	—	−0.7808	—	1.1900	2.1835	4.2760	6.6294	9.7645	13.9355	19.4878	26.9006	36.8477
1.2	−0.5844	—	−1.3607	—	0.6080	1.3899	3.5506	5.8629	8.9493	13.0673	18.564	25.9194	35.8077
1.3	−0.9705	−1.2419	—	—	−0.1600	0.9815	2.8094	5.0900	8.1314	12.1979	17.6396	24.9371	34.7673

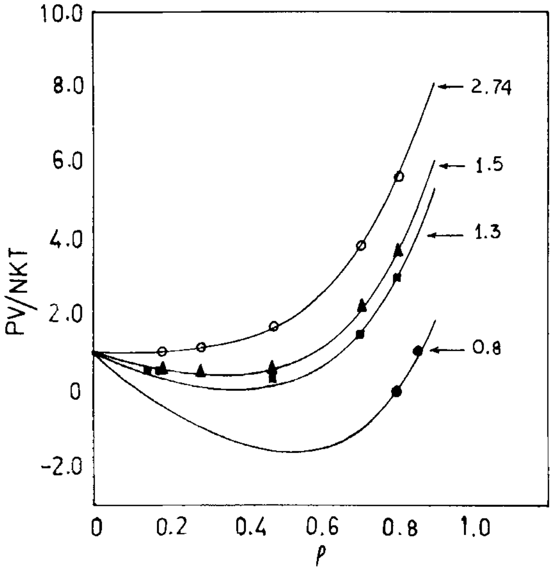

FIGURE 7 Equation of state of TW fluid. The points ○, ▲, ■ and ● give the MC simulation results and the solid curves are isotherms labelled with the appropriate value of T^*.

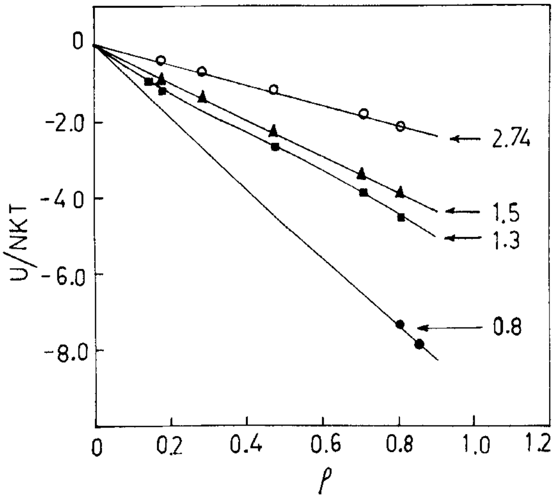

FIGURE 8 Internal energy of a TW fluid. The curves and points have the same meaning as in Figure 7.

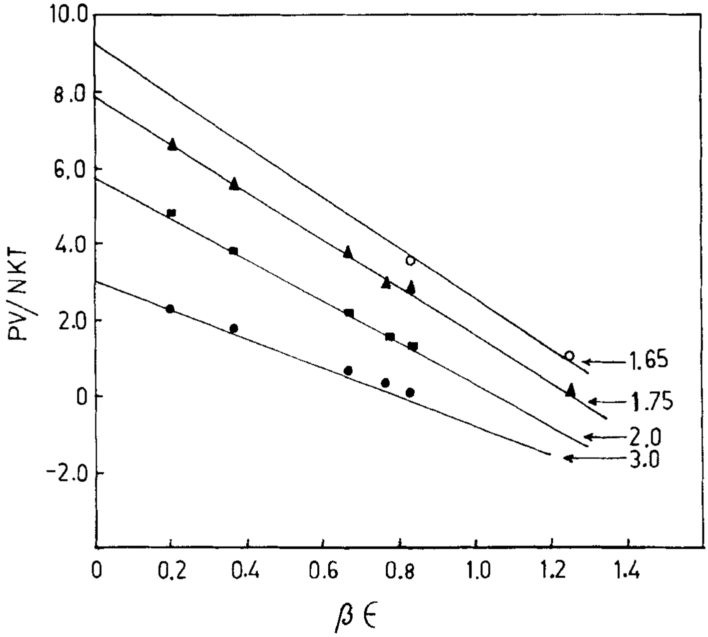

FIGURE 9 Equation of state of TW fluid. The points give the MC simulation results. The curves are isochores labelled with the appropriate value of v/v_0.

results for the isothermal compressibility calculated from the compressibility relation are contained in Table I. As there exists no simulation results, no quantitative test can be made.

The direct correlation function $c(r)$ at two thermodynamic states are shown in Figures 5 and 6. In Figure 7 the pressure calculated from the pressure equation using OCT with the LEXP approximation is compared with the simulation results. The agreement is excellent. Similar conclusions can be drawn from the values of $\langle u \rangle$ displayed in Figure 8.

CONCLUSION

The structure and thermodynamic properties of TW fluid was calculated using various integral equations and the optimised cluster theory. It has been shown that the OCT generates quantitatively the structure and thermodynamic properties of a hard core fluid, e.g. the TW fluid. Of the various integral equations the MSM fails and the PY and HNC equations give qualitatively better results.

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