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Equation of state of a hard-core fluid with a Yukawa tail

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We present Monte Carlo results for the equation of state of a fluid in which the intermolecular potential consists of a hard core of diameter σ and an attractive tail which is of the form of a Yukawa function, $-\epsilon \exp\{-\lambda(r-\sigma)\}/r$ with $\lambda=1{\cdot}8/\sigma$. These results are compared with those obtained from perturbation theory, the mean spherical approximation (MSA), and three related approximation schemes. While perturbation theory works rather well for this system, the MSA is considerably less satisfactory. However, the exponential and linearized exponential modifications of the MSA and the generalized MSA all give good results for this system.

1. INTRODUCTION

The *Ornstein–Zernike* (OZ) *equation* for a simple fluid has the form

$$h_{12}=c_{12}+\rho\int h_{13}c_{32}\,d\mathbf{r}_3, \tag{1}$$

where $h_{12}=h(r_{12})$, etc., and $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$ is the scalar distance between the centres of mass of molecules i and j at position $\mathbf{r}_i$ and $\mathbf{r}_j$. The functions $h(r)$ and $c(r)$ are the *total* and *direct correlation functions*. The total correlation function is related to the radial *distribution function* (RDF), $g(r)$ [the probability density, normalized to unity at large separations, of finding two molecules separated by a distance r], by $g(r)=h(r)+1$. For a fluid with a hard core $h(r)=-1$ inside the hard core.

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While equation (1) is really nothing more than a definition of $c(r)$, which can also be defined graphically [1], its usefulness arises from the fact that in many cases one can obtain a good approximation to $g(r)$ by making a simple ansatz for $c(r)$ and solving (1). Waisman [2] has obtained an analytic solution of equation (1) for the case where $c(r)$ has a 'Yukawa tail', i.e.

$$\left.\begin{aligned} h(r) &= -1, && r<\sigma \\ c(r) &= K\exp\left[-z(r-\sigma)\right]/r, && r>\sigma, \end{aligned}\right\} \tag{2}$$

where σ is the diameter of the hard core of the molecules. This solution is of interest in two contexts. First, consider a fluid with a pairwise additive potential energy for which the intermolecular potential is

$$u(r)=\left\{\begin{aligned} &\infty, && r<\sigma, \\ &w(r), && r>\sigma. \end{aligned}\right\} \tag{3}$$

For such a fluid, the *mean spherical approximation* (MSA) of Lebowitz and Percus [3] consists in assuming

$$c(r)=-\beta w(r), \quad r>\sigma \tag{4}$$

(where $\beta=1/kT$, k is Boltzmann's constant, and T is the temperature) together with the exact condition $h(r)=-1$, $r<\sigma$. Thus, Waisman's solution can be regarded as the solution of the MSA for a fluid for which

$$w(r)=-\epsilon\frac{\exp\left[-\lambda(r-\sigma)\right]}{r/\sigma}, \quad r>\sigma, \tag{5}$$

where the identifications $K=\beta\epsilon$ and $z=\lambda$ are made. Although there is no real fluid with this intermolecular potential, such a fluid could be, for some range of values of λ, a qualitative model of a real fluid.

Secondly, equation (2) can be regarded as the assumed functional form of $c(r)$ for a fluid with some specified intermolecular potential. The parameters K and z are then not given *a priori* in terms of the intermolecular potential but are determined by some semi-empirical method. This type of procedure, first used by Waisman [1] for hard spheres, was formalized by Høye *et al.* [4] in their work on electrolytes. They referred to this as the *generalized mean spherical approximation* (GMSA). It has recently been used by Henderson and Blum [5] to give a good description of the properties of hard spheres and by Waisman *et al.* [6] to describe accurately hard spheres near a hard wall.

Because of these applications, Waisman's solution, which is given in terms of a complex set of simultaneous non-linear equations, has been the object of considerable investigation. Henderson *et al.* [7] have given series expansions in powers of K and ρ for the solution. Høye and Stell [8] have simplified Waisman's solution. Their analysis is particularly useful in the GMSA. If $y=g(\sigma^+)$ and $a=\beta(\partial p/\partial\rho)_T$ (where p is the pressure and $\rho=N/V$ is the density) are known, the Høye–Stell procedure can be used to compute K and z, and thus $c(r)$ and $h(r)$, directly without iteration. In addition, Waisman *et al.* [9], Høye and Stell [10] and Høye and Blum [11] have generalized Waisman's solution to the case where $c(r)$ is given by a linear combination of Yukawa functions.

In this paper we study the thermodynamic properties and radial distribution function of a fluid with a hard core plus a Yukawa tail, i.e. the intermolecular potential is given by (3) and (5). Our interest in this Yukawa fluid is due to the fact that expressions for the density profile of this fluid in the simple external potential corresponding to an idealized wall can be obtained [6, 12, 13]. This paper is a necessary step in our study of the interfacial regions of this fluid. In addition, this system permits a direct comparison of the MSA for a simple fluid with other approximations and with exact (Monte Carlo) results. It should thus be useful in evaluating the strengths and weakness of the MSA and GMSA in treatments of other fluids.

The properties of this model Yukawa fluid are determined by several different methods. In the next section we report results of some Monte Carlo computations. These are the ' experimental ' results. In the following sections we then report results obtained from perturbation theory, the MSA and GMSA. We have found that with $\lambda = 1{\cdot}8/\sigma$, the Yukawa fluid is qualitatively similar to argon for the densities and temperatures of the liquid in equilibrium with its vapour and with about the same potential parameters as the Lennard-Jones potential (i.e. $\epsilon/k \sim 120$ K $\sigma \sim 3{\cdot}4$ Å). All calculations reported here use this value of λ.

2. Monte Carlo calculations

The method employed is identical to that used by Henderson *et al.* [14] in their study of the square-well fluid which was, in turn, essentially the method used by Barker and Henderson [15–17] in their study of hard spheres.

The radial distribution function, the pressure and the internal energy were calculated by averaging over the chain of configurations. The resulting values of $g(r)$ are not given here because of space limitations. However, in table 1 we do give our values for $g(\sigma^+)$. The MC values of pV/NkT and $U_i/N\epsilon$ are given in tables 2 and 3. The uncertainty in pV/NkT and $U_i/N\epsilon$ is approximately 0·05 and 0·005, respectively.

Table 1. Values of $g(\sigma^+)$ for the Yukawa fluid ($\lambda = 1{\cdot}8/\sigma$).

ρ^*	T^*	MC	Pert	MSA	LEXP	EXP and GMSA	Equation (21)
0·4	∞	1·811	1·811	1·768	1·811	1·811	1·811
	2·00	2·128	2·156	1·963	2·166	2·202	2·176
	1·50	2·378	2·292	2·040	2·305	2·376	2·330
	1·00	2·943	2·596	2·222	2·634	2·825	2·717
0·6	∞	2·561	2·561	2·460	2·561	2·561	2·561
	2·00	2·921	2·806	2·561	2·821	2·834	2·815
	1·50	2·966	2·900	2·598	2·916	2·912	2·912
	1·00	3·205	3·104	2·681	3·127	3·140	3·129
0·8	∞	3·971	3·971	3·581	3·971	3·971	3·971
	2·00	4·109	4·141	3·629	4·160	4·165	4·143
	1·50	4·257	4·203	3·646	4·227	4·235	4·204
	1·00	4·490	4·334	3·681	4·365	4·384	4·331
	0·70	4·622	4·517	3·729	4·556	4·600	4·509

Table 2. Values of pV/NkT for the Yukawa fluid ($\lambda=1{\cdot}8/\sigma$).

				MSA		LEXP		EXP		
ρ^*	T^*	MC	Pert	E†	P‡	E†	P‡	E†	P‡	GMSA‡
0·4	∞	2·52	2·518	2·518	2·481	2·518	2·518	2·518	2·518	2·518
	2·00	1·08	1·123	1·122	0·943	1·113	1·093	1·114	1·121	1·122
	1·50	0·69	0·664	0·666	0·422	0·653	0·609	0·657	0·660	0·655
	1·00	−0·21	0·246	−0·229	0·645	−0·244	−0·388	−0·228	−0·258	
0·6	∞	4·22	4·283	4·283	4·091	4·283	4·283	4·283	4·283	4·283
	2·00	2·04	1·985	1·978	1·594	1·977	1·969	1·978	1·985	1·992
	1·50	1·21	1·226	1·219	0·760	1·219	1·195	1·222	1·224	1·235
	1·00	−0·27	−0·281	−0·283	−0·911	−0·271	−0·360	−0·259	−0·289	−0·288
0·8	∞	7·65	7·750	7·750	7·001	7·750	7·744	7·750	7·744	7·750
	2·00	4·27	4·459	4·433	3·476	4·446	4·443	4·446	4·451	4·464
	1·50	3·31	3·368	3·332	2·301	3·353	3·340	3·355	3·354	3·373
	1·00	1·29	1·195	1·137	−0·049	1·185	1·129	1·190	1·160	1·198
	0·70	−1·63	−1·582	−1·668	−3·072	−1·562	−1·722	−1·544	−1·657	−1·594

† Calculated from energy equation.
‡ Calculated from pressure equation.

Table 3. Values of $U_i/N\epsilon$ for the Yukawa fluid ($\lambda=1{\cdot}8/\sigma$).

ρ^*	T^*	MC	Pert	MSA	LEXP	EXP	GMSA
0·4	∞	−2·495	−2·495	−2·513	−2·495	−2·495	−2·495
	2·00	−2·583	−2·552	−2·568	−2·586	−2·592	−2·595
	1·50	−2·622	−2·572	−2·594	−2·626	−2·638	−2·658
	1·00	−2·832	−2·610	−2·665	−2·733	−2·766	
0·6	∞	−3·975	−3·975	−3·995	−3·975	−3·975	−3·975
	2·00	−4·030	−4·006	−4·017	−4·035	−4·037	−4·031
	1·50	−4·051	−4·017	−4·026	−4·058	−4·063	−4·056
	1·00	−4·073	−4·039	−4·050	−4·114	−4·125	−4·145
0·8	∞	−5·573	−5·573	−5·602	−5·573	−5·573	−5·573
	2·00	−5·622	−5·589	−5·608	−5·610	−5·611	−5·598
	1·50	−5·630	−5·594	−5·611	−5·623	−5·625	−5·607
	1·00	−5·635	−5·605	−5·616	−5·651	−5·655	−5·629
	0·70	−5·658	−5·619	−5·624	−5·692	−5·699	−5·672

3. Perturbation theory calculations

One method which has been applied with great success in the theory of dense fluids is to expand $g(r)$ in a perturbation series :

$$g(r)=g_0(r)+\beta\epsilon g_1(r)+\ldots, \tag{6}$$

where $g_0(r)$ is the radial distribution of the system when $\beta\epsilon=0$ (i.e. hard spheres)

which has already been tabulated [15, 16]. The first-order term, $g_1(r)$, can be calculated from the convenient expressions (equations (59) and (66) of reference [16]) of Barker and Henderson. The resulting values of $g_1(r)$, which are exact apart from the statistical uncertainties of the MC method, are listed in table 4. Values for $g_1(r)$ for a high density are plotted in figure 1.

The perturbation expansion of the thermodynamic properties can be obtained from

$$A/NkT = A_0/NkT + \beta\epsilon A_1/NkT + (\beta\epsilon)^2 A_2/NkT + \ldots, \tag{7}$$

where A_0 is the hard-sphere free energy, which is taken to be

$$A_0/NkT = \frac{4\eta - 3\eta^2}{(1-\eta)^2} + \text{ideal gas terms.} \tag{8}$$

Table 4. Values of $g_1(r)$ for the Yukawa fluid ($\lambda = 1{\cdot}8/\sigma$).

r^*/ρ^*	0·2000	0·3000	0·4000	0·5000	0·6000	0·7000	0·8000	0·9000
1·0000	0·7809	0·6834	0·5939	0·5113	0·4338	0·3735	0·3178	0·2636
1·0512	0·6284	0·4509	0·4194	0·3253	0·2483	0·1508	0·0733	0·0266
1·1158	0·4162	0·3312	0·2266	0·1417	0·0845	0·0287	−0·0138	−0·0075
1·1769	0·3111	0·1962	0·1307	0·0369	0·0018	−0·0253	−0·0244	−0·0027
1·2349	0·2098	0·1197	0·0191	−0·0353	−0·0552	−0·0484	−0·0272	−0·0147
1·2903	0·1193	0·0544	−0·0175	−0·0449	−0·0739	−0·0557	−0·0156	−0·0192
1·3435	0·0815	−0·0538	−0·0426	−0·0839	−0·0609	−0·0633	−0·0199	−0·0122
1·3946	0·0682	−0·0326	−0·0628	−0·0744	−0·0760	−0·0550	−0·0216	−0·0138
1·4440	0·0127	−0·0365	−0·0780	−0·0699	−0·0573	−0·0145	−0·0210	−0·0110
1·4916	0·0186	−0·0557	−0·0737	−0·0555	−0·0622	−0·0262	−0·0171	−0·0102
1·5379	0·0081	−0·0587	−0·0827	−0·0459	−0·0401	−0·0179	−0·0168	−0·0060
1·5827	0·0435	−0·0611	−0·0781	−0·0447	−0·0219	−0·0093	−0·0110	−0·0038
1·6263	0·0040	−0·0640	−0·0515	−0·0363	−0·0346	0·0064	−0·0082	0·0016
1·6688	−0·0212	−0·0346	−0·0563	−0·0314	−0·0139	0·0024	0·0007	0·0041
1·7103	−0·0534	−0·0304	−0·0389	−0·0119	−0·0019	0·0058	0·0016	−0·0045
1·7507	−0·0131	−0·0203	−0·0277	−0·0151	0·0215	0·0118	0·0034	0·0116
1·7903	−0·0105	−0·0224	−0·0123	−0·0139	0·0119	0·0057	0·0100	0·0119
1·8289	−0·0091	−0·0225	0·0118	−0·0046	0·0198	0·0203	0·0193	0·0196
1·8668	−0·0241	−0·0026	0·0102	0·0133	0·0249	0·0204	0·0184	0·0168
1·9039	−0·0126	−0·0043	0·0199	0·0310	0·0346	0·0308	0·0182	0·0132
1·9404	0·0130	−0·0118	0·0175	0·0390	0·0352	0·0361	0·0184	0·0043
1·9761	0·0221	0·0166	0·0342	0·0265	0·0468	0·0417	0·0089	0·0025
2·0112	0·0149	0·0245	0·0433	0·0481	0·0242	0·0354	0·0176	0·0025
2·0457	0·0261	0·0051	0·0446	0·0399	0·0451	0·0294	0·0176	−0·0005
2·0797	0·0022	0·0363	0·0367	0·0203	0·0321	0·0307	0·0227	0·0003
2·1131	0·0020	0·0051	0·0526	0·0313	0·0408	0·0107	0·0131	−0·0013
2·1459	0·0240	0·0238	0·0473	0·0371	0·0178	0·0077	0·0016	0·0050
2·1783	0·0236	0·0243	0·0486	0·0152	0·0107	0·0056	0·0094	0·0061
2·2102	−0·0244	0·0255	0·0354	0·0280	0·0166	0·0027	0·0042	0·0046
2·2417	0·0335	0·0154	0·0443	0·0256	0·0084	0·0006	0·0124	0·0079

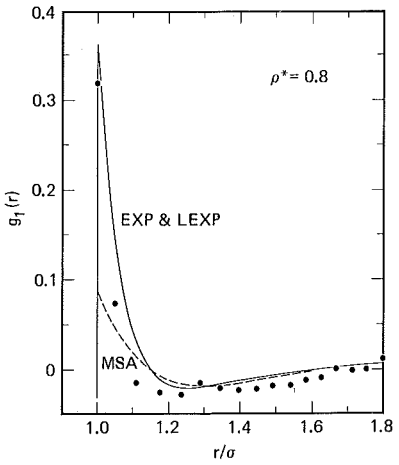

Figure 1. Values for $g_1(r)$ for the Yukawa fluid ($\lambda = 1{\cdot}8/\sigma$) at a high density. The points give the perturbation theory results which are calculated by MC techniques from *exact* expressions. The curves give the results of MSA and its generalizations.

The above expressions result from an integration of the Carnahan and Starling [18] hard-sphere equation of state. The perturbation terms, A_1 and A_2, are obtained from

$$\frac{A_n}{NkT} + \frac{1}{2n}\rho \int w^*(r) g_{n-1}(r)\, d\mathbf{r}, \tag{9}$$

where $w^*(r) = w(r)/\epsilon$. The resulting values have been fitted to the function

$$A_n/NkT = C_n\{1 - \exp\,[-\alpha_n\rho^*/(\beta_n - \rho^*)] - \alpha_n\rho^*/\beta_n\} + P_n\rho^* + Q_n(\rho^*)^2, \tag{10}$$

where $\rho^* = \rho\sigma^3$, for $n = 1$ and 2. We choose $\beta_n = \sqrt{2}$ and force P_n to give the correct contribution in order ρ. The remaining coefficients are chosen by a least-squares criterion. The values of these coefficients for the Yukawa fluid are given in table 5. The final values of A_1 and A_2 are residues resulting from cancellation among the terms in (10). Therefore, the coefficients are given to high accuracy. Values of A_2/NkT are plotted in figure 2. The other thermodynamic properties can be obtained from equation (7) by differentiation. For example, p_n, the nth-order term in a perturbation expansion of the pressure is obtained from A_n by density differentiation.

Table 5. Coefficients in fit of A_1 and A_2 for the Yukawa fluid ($\lambda = 1{\cdot}8/\sigma$)

n	α_n	C_n	P_n	Q_n
1	4·75	0·3150374415	−5·3886151999	−1·1397603697
2	11·25	−0·1401430397	−0·8639815240	−0·1156351900

The A_n, and thus the p_n, calculated from equation (9), are functionals of $g_{n-1}(r)$. However, the p_n can also be calculated from the pressure equation. If this route is taken, the p_n depend on $g_n(\sigma^+)$. Since the $g_n(\sigma^+)$ are difficult to calculate by direct simulation, this pressure equation route is unattractive for

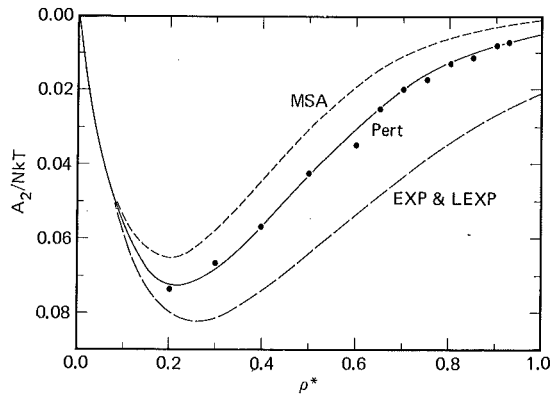

Figure 2. Values of A_2 for the Yukawa fluid ($\lambda = 1{\cdot}8/\sigma$). The points give the perturbation theory results which are calculated by MC techniques from *exact* expressions. The solid curve is a least-squares fit of the MC points and the broken curves give the results of the MSA and its generalizations.

calculation of the p_n. However, the procedure may be inverted to give a method of calculation of the $g_n(\sigma^+)$. Thus,

$$g_n(\sigma^+) = \left(\frac{2\pi\rho^*}{3}\right)^{-1} (p_n V/NkT) + \int_1^\infty (1+\lambda x) \exp\left[-\lambda(x-1)\right] g_{n-1}(x) x \, dx, \quad (11)$$

where p_n is obtained by differentiating A_n. The resulting values of $g_1(\sigma^+)$ and $g_2(\sigma^+)$ are given in tables 4 and 6.

Table 6. Values of $g_2(\sigma^+)$ for the Yukawa fluid ($\lambda = 1{\cdot}8/\sigma$).

ρ^*	$g_2(\sigma^+)$	ρ^*	$g_2(\sigma^+)$
0·2	0·34	0·6	0·10
0·3	0·25	0·7	0·07
0·4	0·19	0·8	0·05
0·5	0·14	0·9	0·03

The perturbation theory value of $g(\sigma^+)$, calculated from

$$g(\sigma^+) = \sum_{n=0}^{2} (\beta\epsilon)^n g_n(\sigma^+), \quad (12)$$

are compared with the MC values in table 1 and the perturbation theory values of pV/NkT and $U_i/N\epsilon$ are compared with MC values in tables 2 and 3, respectively. We have not distinguished whether the perturbation theory values of pV/NkT come from the pressure equation or the energy equation since, if equation (12) is used for $g(\sigma^+)$ and equation (6) is used for $g(r)$, the two equations

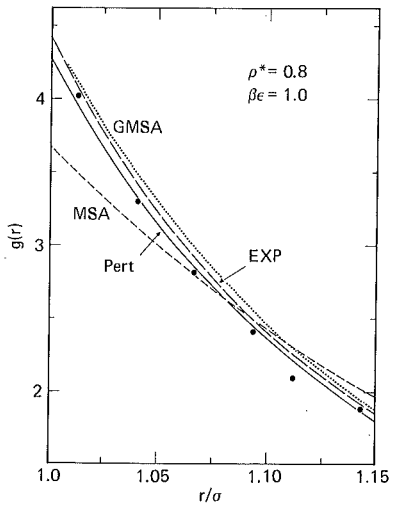

Figure 3. Radial distribution function of the Yukawa fluid ($\lambda = 1{\cdot}8/\sigma$). The points give the MC results and the curves give the results of various approximate theories.

give identical results. In addition, perturbation theory values of $g(r)$ and pV/NkT are plotted in figures 3 and 4. The agreement with the machine simulations is good.

Inasmuch as our main interest is in the interfacial regions of the Yukawa fluid, we give the perturbation theory values of the free energy in table 7. There are no MC values for comparison. However, since the perturbation theory equation of state is seen to be good in table 2 and figure 4, it is reasonable to believe that the perturbation theory values for A are accurate—especially at high densities where the perturbation series converges rapidly.

Table 7. Values of A/NkT for the Yukawa fluid ($\lambda = 1{\cdot}8/\sigma$) (perfect gas terms not included).

ρ^*	T^*	Pert	MSA	LEXP	EXP
0·4	∞	1·130	1·130	1·130	1·130
	2·00	−0·132	−0·139	−0·150	−0·151
	1·50	−0·559	−0·569	−0·859	−0·590
	1·00	−1·422	−1·443	−1·485	−1·493
0·6	∞	2·042	2·042	2·042	2·042
	2·00	0·048	0·039	0·026	0·025
	1·50	−0·620	−0·631	−0·653	−0·654
	1·00	−1·962	−1·976	−2·024	−2·027
0·8	∞	3·403	3·403	3·403	3·403
	2·00	0·613	0·600	0·588	0·588
	1·50	−0·318	−0·334	−0·354	−0·355
	1·00	−2·183	−2·206	−2·246	−2·247
	0·70	−4·586	−4·164	−4·692	−4·695

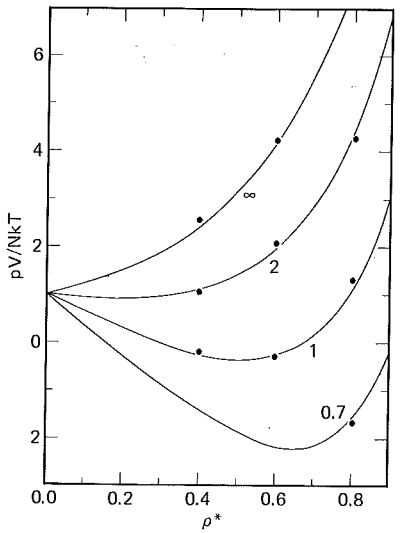

Figure 4. Equation of state of the Yukawa fluid ($\lambda = 1{\cdot}8/\sigma$). The points are the MC values and the curves gives the perturbation theory results.

Once the free energy is known, the vapour pressure can be calculated easily at low temperatures where the vapour has a vanishingly small density. Assuming the vapour to be ideal,

$$\ln p^* = \ln T^* - 1 + A_L/NkT, \tag{13}$$

where $p^* = p\sigma^3/\epsilon$ and $T^* = kT/\epsilon$. The density of the liquid, ρ_L, need not be known exactly before the vapour pressure is calculated. Since the vapour pressure is small, the free energy of the liquid A_L will be roughly constant in the neighbourhood of ρ_L. The perturbation theory values of $\rho_L{}^*$ and p^* are given in table 8 for $T^* = 0{\cdot}8$. We expect that these values are quite reliable. Recently, Adams [19] has made computer simulation studies of the vapour pressure of the Lennard-Jones fluid and has found that perturbation theory gives accurate values of the vapour pressure of a fluid near its triple point. The situation should be even more favourable here because A_2 is smaller relative to A_1 than is the case for the Lennard-Jones fluid. Presumably this means that perturbation theory is even more rapidly convergent for the Yukawa fluid (with $\lambda = 1{\cdot}8/\sigma$) than for the Lennard-Jones fluid.

Table 8. Density and pressure of the Yukawa fluid ($\lambda = 1{\cdot}8/\sigma$) in equilibrium with its vapour at $T^* = 0{\cdot}8$.

	Pert	Exp(E)†	Exp(P)‡	GMSA(P)‡
$\rho_L{}^*$	0·8335	0·8327	0·8375	0·8336
p^*	0·0065	0·0059	~0·006	~0·006

† Calculated from energy equation.
‡ Calculated from pressure equation.

Table 9. Values of critical constants for the Yukawa fluid ($\lambda=1{\cdot}8/\sigma$).

	Pert	GMSA C†	GMSA P‡
T_c^*	1·255	1·255	1·29
ρ_c^*	0·31	0·31	0·27–0·28
P_c^*	0·148	0·148	0·141
P_cV_c/NkT_c	0·38	0·38	0·39–0·40

† Calculated from compressibility equation.
‡ Calculated from pressure equation.

Finally, for completeness the perturbation theory estimates of the critical constants of the Yukawa fluid are given in table 9. There are no machine simulation values for comparison. Since the convergence of perturbation theory is slower at low densities, there are undoubtedly some errors in these perturbation theory estimates. However, the errors should not be large.

4. Mean spherical approximation

As mentioned previously, the MSA for the Yukawa fluid is obtained by combining equations (4) and (5). Given λ and $\beta\epsilon$, the four parameters $a=\beta\partial p/\partial\rho$, b, $v=-2U_i/NkT$, and $y=g(\sigma^+)$ needed for the calculation of the MSA $c(r)$ can be obtained by iteration from Waisman's equations. These equations are not written out fully in reference [2]. However, they appear as equations (6)–(8) and (10)–(12) in reference [7]. (It is to be noted, however, that a rather obvious additive factor of unity is missing from the second half of equation (8) of reference [7].) These factors, a, b, v, and y, can also be determined, again by iteration, from the equations of Høye and Stell [8]. We have compared the exact values of these parameters with those obtained from the inverse temperature expansions given by Henderson *et al.* [7] and have found nearly perfect agreement. Evidently, five terms in a temperature expansion are sufficient for convergence in the MSA for $\lambda=1{\cdot}8$ for all values of T^* and ρ^* which are of interest. When convergent, the expansion is the easiest method of calculating these parameters.

Once a, b, v, and y have been determined, $c(r)$ can be determined. From this, the Fourier transform, $\tilde{c}(k)$, can be determined analytically. Because of the OZ equation

$$\tilde{h}(k)=\frac{\tilde{c}(k)}{1-\rho\tilde{c}(k)}. \tag{14}$$

Thus, all that remains in the determination of $g(r)=1+h(r)$ is the numerical transformation of $\tilde{h}(k)$. Because $h(r)-c(r)$ is continuous, this can be done very accurately by transforming only $\tilde{h}(k)-\tilde{c}(k)$, particularly if only the difference between $\tilde{h}(k)-\tilde{c}(k)$ and $\tilde{h}_0(k)-\tilde{c}_0(k)$, the hard-sphere or infinite temperature result, is transformed numerically. The resulting values of $g(r)$ at $\beta\epsilon=1$ and $\rho^*=0{\cdot}8$ are plotted in figure 3. The contact value is much too low. This is seen further in table 1.

The thermodynamic properties can be calculated from the energy equation, or equivalently from $v=-2U_i/NkT$. These values of $U_i/N\epsilon$ are listed in table 3. The free energy can be obtained from these values of U_i by numerical integration (analytical integration if the temperature expansion is used). The MSA values for the free energy, obtained in this manner, are tabulated in table 7. In most applications the equation of state obtained by differentiating these energy equation values of the free energy are more accurate than those obtained from either the pressure equation or the compressibility, a. Normally this is a cumbersome method of obtaining the equation of state, since the integration and the subsequent differentiation must be done numerically. However, for the particular case of the MSA, Høye and Stell [20] have shown that the energy equation of state can be calculated from

$$\frac{pV}{NkT}=\frac{p_0V}{NkT}+\frac{\pi}{3}\rho^*[g^2(\sigma^+)-g_0^2(\sigma^+)]-\frac{2\pi}{3}\rho^*\beta\epsilon\int_1^\infty\frac{\partial w^*}{\partial x}g(x)x^3\,dx. \qquad (15)$$

This remarkable result permits the calculation of the MSA energy equation of state with no more difficulty than that required from the pressure equation. In fact the integral which appears in (15) is exactly the integral appearing in the pressure equation. The MSA values of pV/NkT, calculated from (15), are listed in table 2.

The MSA values of U_i, A, and p which are calculated from the energy equation are in good agreement with the MC and perturbation theory results. On the other hand, the MSA values of p, calculated from the pressure equation, are significantly in error, as is seen from table 2. This is primarily caused by the values of the MSA $g(\sigma^+)$.

The equation of state can also be calculated from the compressibility equation, i.e. from a. This has not been done because it requires a numerical integration which is inconvenient at high temperatures and which is not possible at temperatures below the critical temperature.

Henderson *et al.* [7] have calculated the MSA values for $g_1(r)$. Their values are plotted in figure 1 for $\rho^*=0{\cdot}8$. The MSA $g_0(r)$ is identical with the Percus–Yevick [21, 22] results for hard spheres. Both $g_0(r)$ and $g_1(r)$ are too small at contact. Thus, it is not surprising that the MSA $g(r)$ is also too small at contact. The terms in the perturbation expansion of the free energy are related to the $g_n(r)$ by equation (9). The errors in the MSA $g_0(r)$ do not result in serious errors in the MSA A_1. However, as is seen in figure 2, the small values of the MSA $g_1(r)$ do result in significant relative errors in A_2. However, the absolute error in the free energy itself is small.

5. LEXP AND EXP MODIFICATIONS OF THE MSA

Andersen *et al.* [23] have proposed the optimized random-phase approximation (ORPA) which consists in replacing equation (4) by

$$c(r)=c_0(r)-\beta w(r), \quad r>\sigma, \qquad (16)$$

where $c_0(r)$ is the *exact* hard-sphere direct correlation function. If equation (16) is combined with the exact condition $h(r)=-1$, $r<\sigma$, the OZ equation can be

solved and $g(r)$ can be calculated. The result for $g(r)$ can be written as

$$g(r)=g_0(r)+\mathscr{C}_L(r), \tag{17}$$

where $g_0(r)$ is the *exact* hard-sphere RDF.

The ORPA is similar to the MSA. In fact the recent calculations of Henderson *et al.* [24] for the square-well potential show that only the hard-sphere part of $g(r)$ is significantly affected by the replacement of (4) by (16). In other words, $\mathscr{C}_L(r)$ may be approximated by the difference of the MSA $g(r)$ and the MSA $g_0(r)$:

$$\mathscr{C}_L(r)\sim g^{MSA}(r)-g_0{}^{MSA}(r). \tag{18}$$

This means that the ORPA shares many of the deficiencies of the MSA. Although $g_0(\sigma^+)$ is given correctly in the ORPA, $g(\sigma^+)$ will still be small.

Andersen *et al.* [23] have proposed the *EXP* (*exponential*) *approximation*

$$g(r)=g_0(r)\exp[\mathscr{C}_L(r)] \tag{19}$$

and the *LEXP* (*linearized exponential*) *approximation*

$$g(r)=g_0(r)[1+\mathscr{C}_L(r)], \tag{20}$$

where $g_0(r)$ in equations (19) and (20) is the *exact* hard-sphere RDF. Both approximations yield a first-order term, $g_1(r)$, which is $g_0(r)$ times the ORPA $g_1(r)$, or, if (18) is used, $g_0(r)$ times the MSA $g_1(r)$. The LEXP and EXP $g_1(r)$, calculated from equation (18), is plotted in figure 1. There is a significant improvement over the MSA values. On the other hand, it is surprising to note that the LEXP and EXP A_2 is, as is seen from figure 2, somewhat worse than the MSA result.

The LEXP and EXP approximation results [again calculating using (18)] are given in tables 1–3 and 7 and in figure 3. Both are improvements over the MSA results. The EXP results are especially good and are somewhat better than the perturbation theory results. This is so despite the fact that the EXP results for $g_1(\sigma^+)$ and A_2 are too large in magnitude. It must, therefore, result from compensations in higher-order terms. Indeed the perturbation theory results, where higher-order terms are neglected, would improve if a larger value of $g_1(\sigma^+)$ and A_2 were used.

The EXP values of the density and pressure of the Yukawa fluid in equilibrium with its vapour at $T^*=0{\cdot}8$ are given in table 8. It is seen that the small differences in the perturbation and EXP free energies (calculated from the energy equation) do not result in significant differences in ρ^* and p^*. Since at high densities the differences in the EXP pressure and energy equations of state are similar in magnitude to the differences between the EXP and perturbation theory equations of state and since these latter differences did not result in significant differences in p^*, we have assumed the EXP pressure equation vapour pressure is about the same as the EXP energy equation value (this is equivalent to assuming that the EXP pressure equation free energy is about the same as the EXP energy equation result) and have calculated the corresponding value of ρ^* using the pressure equation. The value is given in table 8 also.

6. Generalized mean spherical approximation

A final procedure which we examine here is the GMSA where we assume that $c(r)$ has the form given by equation (2) but do *not* make the identifications, $K=\beta\epsilon$ and $z=\lambda$, which are used in the MSA. The most convenient procedure is to use the Høye–Stell equations [8] which give K and z explicitly as functions of $a=\beta\partial p/\partial\rho$ and $y=g(\sigma^+)$. The advantage of the GMSA over the EXP modification of the MSA is that the analytic expression for $c(r)$ is retained. If we wishes to compute $c(r)$ in the EXP approximation we would have to compute first $g(r)$ (ultimately from a numerical Fourier transformation) and then compute the EXP $c(r)$ by further numerical Fourier transformation with possible loss of accuracy. On the other hand, we must know the equation of state before we can use the Høye–Stell procedure. However, this is no problem because as a result of the MC, perturbation, and MSA calculations reported earlier in this paper, we now know the Yukawa fluid equation of state rather well.

To calculate $g(\sigma^+)$, we could require that the pressure and energy equations of state be consistent, or at least nearly so. We have seen that the MSA energy equations of state is very accurate. Thus if we neglect the change in the energy equation of state and the change in the integrals in the pressure and energy equations in passing from the MSA to the GMSA, we obtain

$$g(\sigma^+)=g_0(\sigma^+)+\tfrac{1}{2}\{[g^{\mathrm{MSA}}(\sigma^+)]^2-[g_0{}^{\mathrm{MSA}}(\sigma^+)]^2\}, \tag{21}$$

where $g_0(\sigma^+)$ is the *exact* hard-sphere RDF obtained from MC results. In principle, equation (21) could be generalized into an iterative procedure whereby the pressure and energy equations of state could be made fully self-consistent. However, it is awkward to do so because equation (15) is valid only in the MSA. However, use of equation (15) should result in near self-consistency.

The values of $g(\sigma^+)$ calculated from equation (21) are listed in table 1. They are somewhat inferior to those obtained from the EXP approximation. Because of this we use the EXP values of $g(\sigma^+)$ in this work.

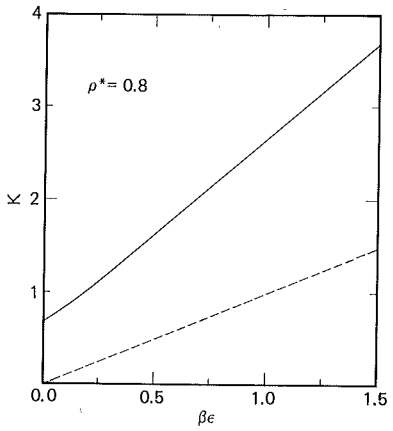

Figure 5. Temperature variation of K in the MSA and GMSA. The solid and broken lines give the GMSA and MSA results, respectively.

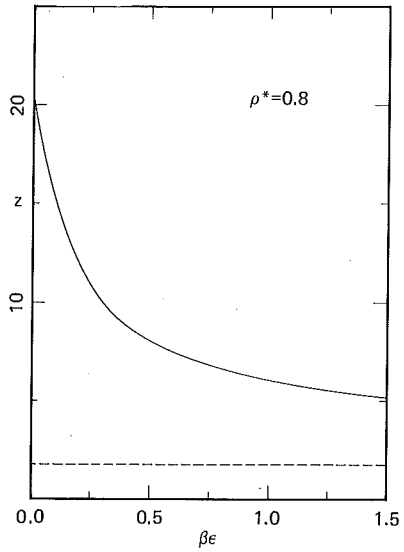

Figure 6. Temperature variation of z in the MSA and GMSA. The curves have the same meaning as in figure 5.

We can calculate a by differentiating the MSA energy equation of state. Since the perturbation theory and MSA energy equation of state results are so similar it is equivalent, but more convenient, to differentiate the perturbation theory pressures, since the perturbation theory equation of state is analytic.

Now that a and y are determined, K and z can be determined from the Høye–Stell procedure. The resulting values of K and z have been given, for $\beta\epsilon = 0$, by Henderson and Blum [5]. The temperature dependence of K and z are given for $\rho^* = 0{\cdot}8$ in figures 5 and 6. As $\beta\epsilon$ increases, K increases in an approximately linear fashion. On the other hand, z decreases towards the MSA values as $\beta\epsilon$ increases. The temperature dependence of K and z is qualitatively similar at other densities.

The GMSA results are given in tables 1–3 and in figure 3. We have not calculated the energy equation of state, as this would require extensive calculations and presumably would result in values which are much the same as the perturbation theory, LEXP, and EXP energy equations of state already reported here. On the other hand, the GMSA pressure equation of state is slightly better than the EXP pressure equation of state.

The GMSA pressure equation estimate the pressure and density of the Yukawa fluid in equilibrium with its vapour are given in table 8. Again we have assumed that the GMSA pressure equation of state value of the free energy is about the same as the perturbation theory or EXP energy equation of state values. This should be a very good approximation.

The GMSA critical point results are given in table 9. The GMSA compressibility equation results will be identical to the perturbation theory results because of our procedure for choosing a. The GMSA pressure equation results are very similar. Presumably the GMSA energy equation results would also be very similar.

7. Summary

Monte Carlo results for the equation of state of a fluid with a hard core and an attractive Yukawa tail have been given for the case where the decay parameter, λ, of the Yukawa tail is $1{\cdot}8/\sigma$.

In addition, perturbation theory and the mean spherical approximation are applied to this system. Perturbation theory works well. The MSA is less satisfactory. However, modifications of the MSA which do give satisfactory results are considered. Of these the GMSA has the great advantage of giving analytic expressions for most quantities of interest.

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