A new thermodynamic model for the hard-core fluid with a Yukawa tail[a)]

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A new and analytical thermodynamic model for simple fluids with an intermolecular pair potential consisting of a hard-sphere core and an attractive Yukawa tail is presented. The model yields simple analytic expressions for all thermodynamic properties of the fluid system. The self-consistent numerical results of the present model for the compressibility factor, internal energy, and Helmholtz free energy are in excellent agreement with the Monte Carlo "experiments" for the whole range of temperatures and densities in which experimental data are available.

I. INTRODUCTION

The theory of simple fluids with spherical potentials is rather well developed and little remains to be done as far as improving the agreement with known experiments (real life and computer calculations) are concerned. However, most of these theoretical models involve extensive numerical computations and are often not practical for obtaining quick and accurate results for real fluids. It is therefore of great interest to be able to condense numerical results of long tables into simple analytical expressions that not only are simpler to handle, but also give physical insights that could provide a basis for applications and extensions to more complicated fluid systems. A technique of this nature is the solution of the mean spherical approximation (MSA)[1] for a hard sphere fluid with a Yukawa tail recently obtained by Waisman,[2] which was later extended by Høye and Stell[3(a)] and generalized by Høye *et al.*[3(b)] in their work on electrolytes and generalized mean spherical approximation. Waisman's solution, which is given in terms of a complex set of simultaneous nonlinear equations, has also been generalized[4] to the case of a linear combination of Yukawa functions. However, the increasing number of the closed form algebraic equations and their highly nonlinear nature make the theory computationally impracticable for pair potentials with more than one Yukawa term.

The primary goal of the work presented in this paper has been to develop within the framework of MSA a simple and analytical thermodynamic model for fluids with pair potentials of Yukawa form, outside a hard-sphere core, which would enable one to perform accurate self-consistent calculations of the thermodynamic properties of pure fluids and fluid mixtures. Furthermore, the results herein for the single Yukawa term can be easily generalized to an arbitrary number of Yukawas, without introducing any further computational difficulty. The single Yukawa term fluid, however, permits a direct comparison of our model with other approximations and with the exact (Monte Carlo) results.[5] It should thus be useful in evaluating the strengths and weaknesses of the model in treatments of other more complex fluids.

In Sec. II we introduce the model which is based on approximating the exact radial distribution function (RDF) of the hard-core Yukawa fluid with the Percus–Yevich (PY) RDF for hard spheres,[6] provided that an appropriate state-dependent "effective hard-sphere" reduced density η can be self-consistently determined. In Sec. III we show how one can determine η using thermodynamic consistency. Our numerical results of the thermodynamic properties are presented and compared with the Monte Carlo results, perturbation theory and other related schemes, in Sec. IV.

II. DERIVATION OF THE MODEL

We consider a fluid with a pairwise additive potential energy for which the intermolecular potential consists of a hard core and an attractive Yukawa tail of the form

$$\phi(r) = \begin{cases} \infty, & r \le \sigma, \\ -\epsilon \dfrac{\exp[\kappa(\sigma - r)]}{r/\sigma}, & r > \sigma, \end{cases} \tag{1}$$

where σ is the diameter of the hard core of the molecules. The excess internal energy per particle, Δu, for spherical potentials is given by the general energy equation

$$\Delta u \equiv N^{-1}\Delta U = 2\pi\rho \int_0^\infty g(r)\phi(r)r^2\, dr, \tag{2}$$

where $g(r)$ is the exact radial distribution function of the fluid system. The term "excess" denotes the actual value of a quantity minus the perfect gas value at the same density ρ and temperature T.

Høye and Stell[7] have shown that within the MSA the energy equation of state of a fluid with a hard core can be calculated from

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$$\frac{P}{\rho kT}=\frac{P_0}{\rho kT}+\frac{\pi}{3}\rho\sigma^3[g^2(\sigma^+)-g_0^2(\sigma^+)]-\frac{2\pi\rho}{3kT}\int_\sigma^\infty g(r)\frac{d\phi(r)}{dr}r^3\,dr, \quad (3)$$

where P_0 and $g_0(\sigma^+)$ are the pressure and contact value of the radial distribution function of the hard-sphere reference system, respectively. (We shall use the subscript 0 throughout to denote hard-sphere quantities.)

By substituting Eq. (1) into Eqs. (2) and (3) we find

$$\Delta u=-2\pi\epsilon e^z\rho^*\int_1^\infty xg(x)e^{-zx}dx \equiv -2\pi\epsilon e^z\rho^*\hat{g}(z) \quad (4)$$

and

$$\frac{P}{\rho kT}=\frac{P_0}{\rho kT}+\frac{\pi}{3}\rho^*[g^2(1^+)-g_0^2(1^+)]+\frac{2\pi\epsilon\rho^*}{3T^*}[z\hat{g}'(z)-\hat{g}(z)], \quad (5)$$

where we have used the dimensionless quantities $x \equiv r/\sigma$, $z \equiv \kappa\sigma$, $\rho^*=\rho\sigma^3$, and $T^*=kT/\epsilon$. The integral in Eq. (4) is the Laplace transform, $\hat{g}(s)$, of $xg(x)$ for $x=z$, and $\hat{g}'(z)=[d\hat{g}(s)/ds]_{s=z}$. (The prime above and throughout the rest of this article denotes differentiation with respect to the argument of the function.) For the hard-sphere reference system we use the Carnahan and Starling[8] expressions,

$$\frac{P_0}{\rho kT}=\frac{1+\theta+\theta^2-\theta^3}{(1-\theta)^3} \quad (6)$$

for the equation of state, and

$$g_0(1^+;\theta)=\frac{2-\theta}{2(1-\theta)^3} \quad (7)$$

for the contact value of the radial distribution function, where the reduced density θ is

$$\theta=\pi\rho\sigma^3/6=\pi\rho^*/6. \quad (8)$$

At this stage we approximate in our model the exact RDF, $g(x)$, with the Percus–Yevick RDF, $g_0(x)$, for hard spheres. The Laplace transform, $\hat{g}_0(z)$, of $g_0(x)$ is then given by Wertheim's[6] analytic solution,

$$\hat{g}_0(z)=zf_1(\eta;z), \quad (9)$$

where

$$f_1(\eta;z)=\frac{L(\eta;z)}{12\eta L(\eta;z)+S(\eta;z)e^z}, \quad (10a)$$

$$L(\eta;z)=(1+\eta/2)z+1+2\eta, \quad (10b)$$

$$S(\eta;z)=(1-\eta)^2z^3+6\eta(1-\eta)z^2+18\eta^2z-12\eta(1+2\eta), \quad (10c)$$

and

$$\eta\equiv\pi\rho d^3/6. \quad (11)$$

The reduced density η and the corresponding hard-sphere diameter d will then be considered as "state-dependent effective hard-particle" quantities, the values of which we expect to depend on both the density and temperature, and must therefore be determined self-consistently. As a result of the above approximation the contact value $g(1^+)$ in Eq. (5) will then be equal to $g_0(1^+;\eta)$ given by Eq. (7), but with θ replaced by η.

Upon substituting Eqs. (6) and (9) into (4) and (5), we find the expressions

$$\Delta u=\rho F(\eta) \quad (12)$$

and

$$\frac{P}{\rho kT}=\frac{1+\theta+\theta^2-\theta^3}{(1-\theta)^3}+\frac{\pi}{3}\rho^*[g_0^2(1^+;\eta)-g_0^2(1^+;\theta)]+\frac{2\pi z^2e^z\rho^*}{3T^*}f_2(\eta;z), \quad (13)$$

where

$$F(\eta)=-2\pi\epsilon\sigma^3ze^zf_1(\eta;z), \quad (14a)$$

$$f_2(\eta;z)=\partial f_1(\eta;z)/\partial z = e^z\{L_z(\eta;z)S(\eta;z)-L(\eta;z)[S(\eta;z)+S_z(\eta;z)]\} \div \{12\eta L(\eta;z)+S(\eta;z)e^z\}^2, \quad (14b)$$

$$L_z(\eta;z)\equiv\partial L(\eta;z)/\partial z=1+\eta/2, \quad (14c)$$

and

$$S_z(\eta;z)\equiv\partial S(\eta;z)/\partial z=3(1-\eta)^2z^2+12\eta(1-\eta)z+18\eta^2. \quad (14d)$$

It is important to note that as a result of approximating $\hat{g}(z)$ with $\hat{g}_0(z;\eta)$, the ratio $\Delta u/\rho$ depends on ρ and T only through the single parameter η. This is analogous to Wertheim's[9] model for classical fluids, in which $\Delta u/\rho$ depends only on Ω, where $\Omega=\eta/\rho$ was considered as an "effective hard-particle volume." Equations (12)–(14) constitute the basic equations for determining the internal energy and compressibility factor for the hard-core Yukawa fluid, provided that the reduced density η is known as a function of density and temperature.

III. SELF-CONSISTENT DETERMINATION OF $\eta(\rho, T)$

In this section we show how one can analytically determine $\eta(\rho, T)$ by imposing thermodynamic self-consistency between the expressions relating the derivatives of the Helmholtz free energy with the internal energy and pressure. The next question that arises then is the choice of the functional form of the entropy of the hard-core Yukawa fluid.

In analogy with Wertheim's model[9] we model the excess entropy for the Yukawa fluid, $\Delta s=N^{-1}\Delta S$, on the excess entropy for hard spheres, which is of the form $\Delta s=\Delta s(\eta_s)$. This assumption is consistent with conclusions of the VIM theory of molecular thermodynamics in which the excess entropy of a real fluid is shown to be equal to that of a hard-sphere fluid with a temperature and density dependent diameter.[10,11] Here, $\eta_s=\pi\rho d_s^3/6$ is a state-dependent "effective hard-particle dimensionless density," analogous to η, and must also be determined self-consistently as a function of density and temperature. We use the Carnahan and Starling expression for Δs which is given by

$$\Delta s \equiv -kG(\eta_s) = -k\frac{\eta_s(4-3\eta_s)}{(1-\eta_s)^2}. \quad (15)$$

From Eqs. (12) and (15) it immediately follows that

$$\alpha \equiv N^{-1}\beta\Delta A = \beta\rho F(\eta) + G(\eta_s), \quad (16)$$

where $\beta = (kT)^{-1}$ and ΔA is the excess Helmholtz free energy.

Thermodynamic consistency requires that the relation

$$\Delta u = [\partial\alpha/\partial\beta]_\rho \quad (17)$$

be satisfied. Applying Eq. (17) to Eq. (16) one finds

$$\beta\rho F'(\eta)[\partial\eta/\partial\beta]_\rho + G'(\eta_s)[\partial\eta_s/\partial\beta]_\rho = 0. \quad (18)$$

Furthermore, thermodynamic consistency requires that the excess pressure is given by

$$\Delta P = \rho^2[\partial(\Delta A)/\partial\rho]_\beta. \quad (19)$$

Applying Eq. (19) to Eq. (16) one finds

$$\Delta P/\rho^2 = F(\eta) + \rho F'(\eta)[\partial\eta/\partial\rho]_\beta + \beta^{-1}G'(\eta_s)[\partial\eta_s/\partial\rho]_\beta. \quad (20)$$

This completes the thermodynamic consistency, i.e., Eqs. (18) and (20) consist of the basic equations for determining η and η_s.

In the high temperature regime ($\epsilon\beta \to 0$), the structure of the real fluid should be the same as that of the hard-sphere reference system, and hence one expects both η and η_s to approach the hard-sphere parameter θ [Eq. (8)] in this limit. Note that in this limit, Eq. (13) reduces to

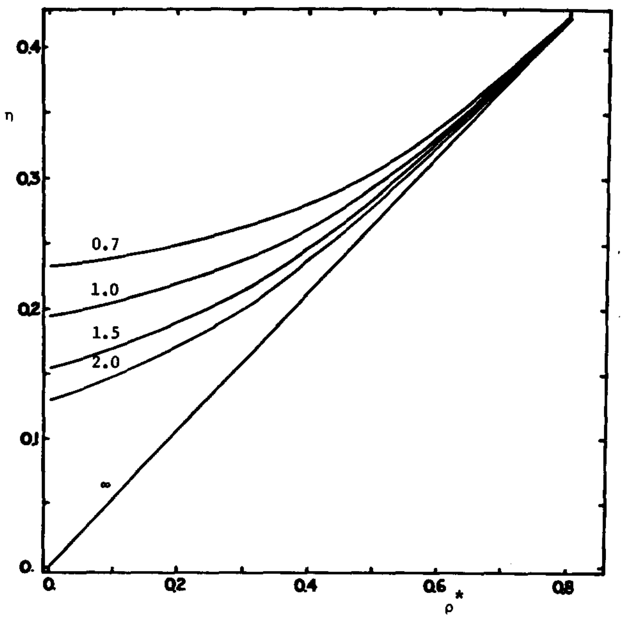

FIG. 1. Effective hard-sphere reduced density η of the Yukawa fluid, as a function of $\rho^* = \rho\sigma^3$, with $z = 1.8$, for five different isotherms labeled with the appropriate values of $T^* = kT/\epsilon$.

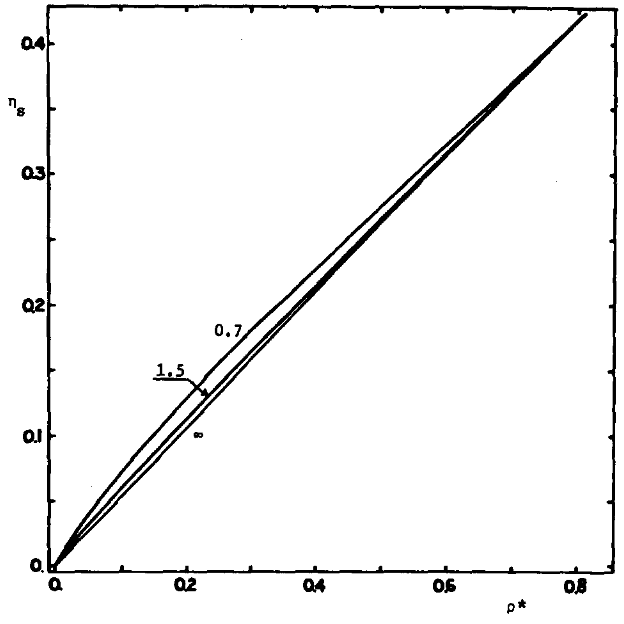

FIG. 2. Effective hard-sphere parameter η_s of the Yukawa fluid, as a function of $\rho^* = \rho\sigma^3$, with $z = 1.8$, for three different isotherms labeled with the appropriate values of $T^* = kT/\epsilon$.

the equation of state for hard spheres. Thus, one can perform a perturbation expansion of these quantities in powers of $\epsilon\beta$, of the form

$$\eta(\rho, \beta) = \theta(\rho) + \sum_{K=1}^{\infty} (\beta\epsilon)^K \eta_K(\rho) \quad (21a)$$

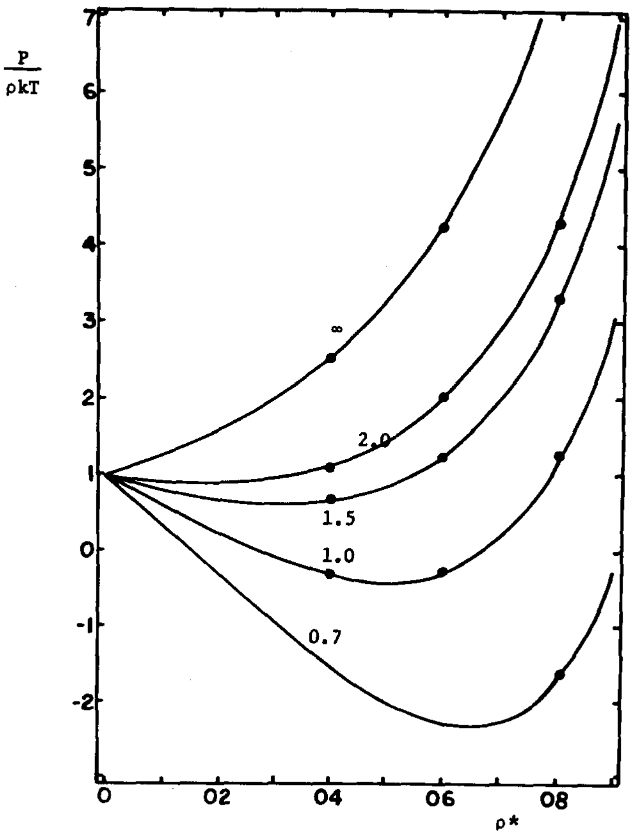

FIG. 3. Equation of state for the Yukawa fluid with $z = 1.8$. The curves are isotherms as labeled with T^*, the reduced temperature. They are calculated from Eq. (13) using the self-consistently determined values of $\eta(\rho, T)$. The points are the Monte Carlo values.

TABLE I. Values of $P/\rho kT$ for the Yukawa fluid with $z = 1.8$.

				MSA[c]		LEXP[c]		EXP[c]			
ρ^*	T^*	MC[5]	Pert[5]	E[a]	P[b]	E	P	E	P	GMSA[c]	Present model
0.4	∞	2.52	2.518	2.518	2.481	2.518	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	1.101
	1.50	0.69	0.664	0.666	0.422	0.653	0.609	0.657	0.660	0.655	0.627
	1.00	−0.21	−0.246	−0.229	0.645	−0.244	−0.388	−0.228	−0.258		−0.322
0.6	∞	4.22	4.283	4.283	4.091	4.283	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	1.966
	1.50	1.21	1.226	1.219	0.760	1.219	1.195	1.222	1.224	1.235	1.196
	1.00	−0.27	−0.281	−0.283	−0.911	−0.271	−0.360	−0.259	−0.289	−0.288	−0.343
0.8	∞	7.65	7.750	7.750	7.001	7.750	7.744	7.750	7.744	7.750	7.750
	2.00	4.27	4.459	4.433	3.476	4.446	4.443	4.446	4.451	4.464	4.428
	1.50	3.31	3.368	3.332	2.301	3.353	3.340	3.355	3.354	3.373	3.323
	1.00	1.29	1.195	1.137	−0.049	1.185	1.129	1.190	1.160	1.198	1.114
	0.70	−1.63	−1.582	−1.668	−3.072	−1.562	−1.722	−1.544	−1.657	−1.594	−1.721

[a] E calculated from energy equation.
[b] P calculated from pressure equation.
[c] Reference 5.

and

$$\eta_s(\rho, \beta) = \theta(\rho) + \sum_{K=1}^{\infty} (\beta\epsilon)^K \eta_{Ks}(\rho). \tag{21b}$$

Upon differentiating Eqs. (21a) and (21b) and inserting the resultant expressions in the basic equations (18) and (20), one obtains

$$\sum_{K=1}^{\infty} K(\beta\epsilon)^K [\beta\rho F'(\eta)\eta_K(\rho) + G'(\eta_s)\eta_{Ks}(\rho)] = 0 \tag{22}$$

and

$$\Delta P/\rho kT = \beta\rho[F(\eta) + \theta F'(\eta)] + \theta G'(\eta_s) + \rho \sum_{K=1}^{\infty} (\beta\epsilon)^K \times [\beta\rho F'(\eta)\eta'_K(\rho) + G'(\eta_s)\eta'_{Ks}(\rho)], \tag{23}$$

respectively.

Truncating the perturbation expansion to the first order in η and η_s (which should be valid at least for small values of $\beta\epsilon$), and assuming that both correction terms $\eta_1(\rho)$ and $\eta_{1s}(\rho)$ vary linearly with density, i.e.,

$$\eta_1(\rho) = \alpha_1 \rho^* \tag{24a}$$

and

$$\eta_{1s}(\rho) = \alpha_{1s}\rho^*, \tag{24b}$$

where the parameters α_1 and α_{1s} must be determined self-consistently, Eqs. (22) and (23) assume the simple form

$$\beta\rho F'(\eta)\eta_1(\rho) + G'(\eta_s)\eta_{1s}(\rho) = 0 \tag{25}$$

and

$$P/\rho kT = 1 + \beta\rho[F(\eta) + \theta F'(\eta)] + \theta G'(\eta_s) = \frac{1 + \theta + \theta^2 - \theta^3}{(1-\theta)^3} + \frac{\pi\rho^*}{3}[g_0^2(1^+;\eta) - g_0^2(1^+;\theta)] + \frac{2\pi z e^z \rho^*}{3T^*} f_2(\eta; z). \tag{26}$$

TABLE II. Values of $\Delta U/N\epsilon$ for the Yukawa fluid with $z = 1.8$.

ρ^*	T^*	MC[a]	Pert[a]	MSA[a]	LEXP[a]	EXP[a]	GMSA[a]	Present model
0.4	∞	−2.495	−2.495	−2.513	−2.495	−2.495	−2.495	−2.513
	2.00	−2.583	−2.552	−2.568	−2.586	−2.592	−2.595	−2.554
	1.50	−2.622	−2.572	−2.594	−2.626	−2.638	−2.658	−2.567
	1.00	−2.832	−2.610	−2.665	−2.733	−2.766		−2.590
0.6	∞	−3.975	−3.975	−3.995	−3.975	−3.975	−3.975	−3.995
	2.00	−4.030	−4.006	−4.017	−4.035	−4.037	−4.031	−4.014
	1.50	−4.051	−4.017	−4.026	−4.058	−4.063	−4.056	−4.020
	1.00	−4.073	−4.039	−4.050	−4.114	−4.125	−4.145	−4.032
0.8	∞	−5.573	−5.573	−5.602	−5.573	−5.573	−5.573	−5.602
	2.00	−5.622	−5.589	−5.608	−5.610	−5.611	−5.598	−5.607
	1.50	−5.630	−5.594	−5.611	−5.623	−5.625	−5.607	−5.609
	1.00	−5.635	−5.605	−5.616	−5.651	−5.655	−5.629	−5.613
	0.70	−5.658	−5.619	−5.624	−5.692	−5.699	−5.672	−5.618

[a] Reference 5.

TABLE III. Values of $\Delta A/NkT$ for the Yukawa fluid with $z = 1.8$.

ρP	T^*	Pert[a]	MSA[a]	LEXP[a]	EXP[a]	Present model
0.4	∞	1.130	1.130	1.130	1.130	1.130
	2.00	−0.132	−0.139	−0.150	−0.151	−0.127
	1.50	−0.559	−0.569	−0.859	−0.590	−0.546
	1.00	−1.422	−1.443	−1.485	−1.493	−1.386
0.6	∞	2.042	2.042	2.042	2.042	2.042
	2.00	0.048	0.039	0.026	0.025	0.045
	1.50	−0.620	−0.631	−0.653	−0.654	−0.621
	1.00	−1.962	−1.976	−2.024	−2.027	−1.953
0.8	∞	3.403	3.403	3.403	3.403	3.403
	2.00	0.613	0.600	0.588	0.588	0.602
	1.50	−0.318	−0.334	−0.354	−0.355	−0.332
	1.00	−2.183	−2.206	−2.246	−2.247	−2.199
	0.70	−4.586	−4.164	−4.692	−4.695	−4.599

[a] Reference 5.

Note that the second equality in Eq. (26) follows immediately from Eq. (13). Equations (25) and (26) consist of a set of nonlinear equations to be solved for the correction terms η_1 and η_{1s}.

IV. NUMERICAL RESULTS AND COMPARISON WITH OTHER MODELS

In this section we present the numerical results for thermodynamic properties of the Yukawa fluid based on the present model, and compare them with those obtained by Henderson *et al.*,[5] using the Monte Carlo (MC) computations, perturbation theory, the MSA, the generalized mean spherical approximation (GMSA), the exponential approximation (EXP), and the linearized exponential approximation (LEXP). All calculations reported here have been obtained with $\kappa = 1.8/\sigma$ or $z = \kappa\sigma = 1.8$. As was reported by Henderson *et al.* the Yukawa fluid with this value of κ is qualitatively similar to argon for the densities and temperatures of the liquid in equilibrium with its vapor.

The self-consistent values of η and η_s calculated from solving Eqs. (25) and (26) are plotted in Figs. 1 and 2, respectively, as functions of reduced density for different isotherms. Note that at high densities both values of η and η_s approach the corresponding hard-sphere values. However, at lower densities ($\rho^* \to 0$) η_s approaches zero, whereas η attains a finite value. Having determined the values of η and η_s, one can easily calculate from Eqs. (12), (13), (16), and (7) the excess internal energy, compressibility factor, excess Holmholtz free energy, and the contact value of the RDF.

The calculated values of the compressibility factor are plotted vs density in Fig. 3 for five different isotherms, and are compared with the MC and the perturbation theory values in Table I. The uncertainty in the MC values of $P/\rho kT$ is approximately 0.05. The agreement of the present calculations with both machine simulations and perturbation theory is excellent for $T^* \geq 1.5$ and for the whole range of ρ^*. The rather small values of $P/\rho kT$ at $T^* = 1$ arises from concellation effects between the terms on the right-hand side of Eq. (13). Changes in the value of η of the order of 1% to 2% can lead to changes in $P/\rho kT$ of the order of 20%. Also for comparison, listed in Table I are the MSA, GMSA, EXP, and LEXP values of $P/\rho kT$ calculated from the energy and pressure equations, respectively.[5] Overall our numerical results are in very good agreement with those of the above models. Note that the MSA values of $P/\rho kT$ calculated from the energy equation are in good agreement with the MC and perturbation theory results, whereas those calculated from the pressure equation are significantly in error.

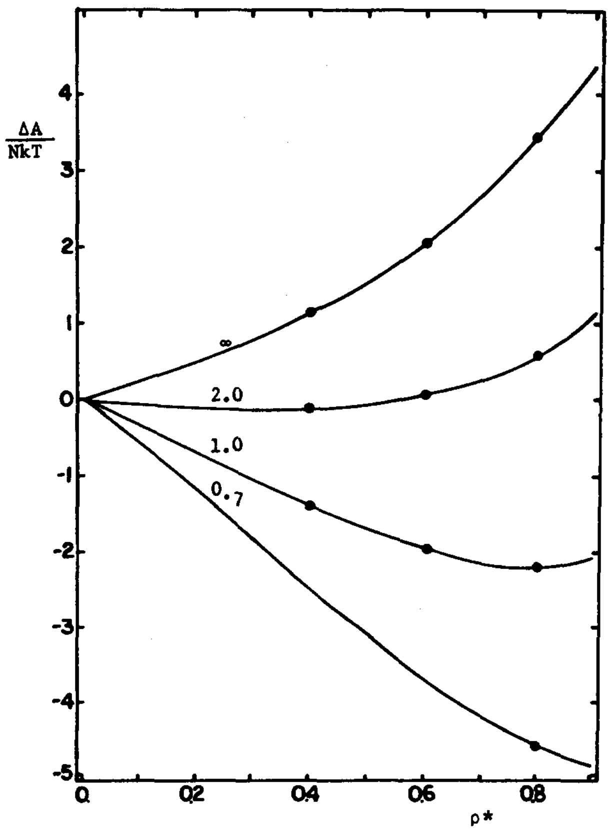

FIG. 4. Calculated values of $\Delta A/NkT$, where ΔA is the excess Helmholtz free energy vs reduced density for the Yukawa fluid ($z = 1.8$) for four isotherms labeled with the appropriate value of T^*. The points are the perturbation theory results of Henderson *et al.*

TABLE IV. Contact values of the radial distribution function, $g(1^+)$, for the Yukawa fluid with $z = 1.8$.

ρ^*	T	MC[a]	Pert[a]	MSA[a]	LEXP[a]	EXP & GMSA	Present model
0.4	∞	1.811	1.811	1.768	1.811	1.811	1.812
	2.00	2.128	2.156	1.963	2.166	2.202	1.986
	1.50	2.378	2.292	2.040	2.305	2.376	2.045
	1.00	2.943	2.596	2.222	2.634	2.825	2.162
0.6	∞	2.561	2.561	2.460	2.561	2.561	2.613
	2.00	2.921	2.806	2.561	2.821	2.834	2.704
	1.50	2.966	2.900	2.598	2.916	2.912	2.735
	1.00	3.205	3.104	2.681	3.127	3.140	2.801
0.8	∞	3.971	3.971	3.581	3.971	3.971	4.028
	2.00	4.109	4.141	3.629	4.160	4.165	4.070
	1.50	4.257	4.203	3.646	4.227	4.235	4.084
	1.00	4.490	4.334	3.681	4.365	4.348	4.113
	0.70	4.622	4.517	3.729	4.556	4.600	4.151

[a] Reference 5.

In Table II, we list the calculated values of $\Delta U/N\epsilon$ which are also in very good agreement with the corresponding MC, perturbation theory, MSA, LEXP, and GMSA results. The uncertainty in the MC values of $\Delta U/N\epsilon$ is approximately 0.005. Our numerical results for the excess Helmholtz free energy are listed in Table III and are plotted in Fig. 4 vs density for four isotherms. There are no MC values of the Helmholtz free energy for comparison. However, since the perturbation theory equation of state is seen to be good in Table I, it is reasonable to believe that the perturbation theory values for ΔA are accurate. The agreement of the present calculations with the perturbation theory results is excellent. Finally, the calculated values for $g(1^+)$ are given in Table IV along with those of the other models. As one would have expected, our results are identical to the MSA results, which are in turn too low compared to those of the MC calculations.

The above comparisons and results indicate that the present model yields very good results for the thermodynamic properties of the single term hard-sphere Yukawa fluid at all ranges of temperature and density, and rather poor results for the contact value of the RDF. The present formalism can be easily generalized to an arbitrary number of Yukawa terms, provided that the Yukawa parameters are known. Extension of the present model to the more complicated cases of polar fluids and fluid mixtures will be reported in a forthcoming paper.

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