

## EQUATION OF STATE OF A HARD CORE FLUID WITH A YUKAWA TAIL

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It appears that for the hard-core potential with Yukawa tail,  $-\varepsilon \exp[-z(x-1)]/x$ , thermodynamic properties calculated through the variational theory are obtainable in almost fully analytic form with the use of hard-core fluid as the reference system. For one negative Yukawa tail minimization of the right-hand side of the variational inequality for the Helmholtz free energy gives diameters of hard-cores of both systems equal, independently of the temperature and the density. Therefore, the whole scheme of calculations is equivalent to adopting the first order Zwanzig  $1/T$  expansion. Comparison with recent calculations of properties of Yukawa system with  $z = 1.8$  presented by Henderson et al. (*Mol. Phys.* **35**, 241 (1978)) shows that our results for free energy are very good, mainly due to the smallness of the  $A_2$  term for this system. The promising features of the variational method for other Yukawa type potentials are outlined.

### 1. Introduction

There is a steadily growing interest in properties of a hard-core fluid with Yukawa tail potential, i.e.

$$u(x) = \begin{cases} \infty, & x < 1, \\ -\frac{\varepsilon}{x} \exp[-z(x-1)], & x > 1, \end{cases} \quad (1)$$

$x = r/\sigma$ , where  $\sigma$  is the diameter of the hard-core of the molecules. For one thing this is because of the existence of Waisman's [1] analytic solution of direct correlation function  $c(r)$  for this potential in the mean spherical approximation [2] (MSA) defined by

$$c(r) = -\beta u(r), \quad r > \sigma \quad (2)$$

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( $\beta = 1/kT$ ,  $T$  is the temperature) with the exact boundary condition  $h(r) = -1$ , where  $h(r)$ , the total correlation function, is connected with  $c(r)$  through the Ornstein-Zernike equation

$$h(r) = c(r) + \rho \int h(|r'|)c(|r-r'|)dr'. \quad (3)$$

Considerable progress on the way of handling complex set of nonlinear equations resulting from Waisman's solution and calculation of various thermodynamic properties was made by Henderson et al. [3] and Høye and Stell [4, 5]. In addition Waisman et al. [6], Høye and Blum [7] and Blum and Høye [8] have derived MSA solutions for linear combination of Yukawa functions, and mixtures. It should be also mentioned that the Yukawa potential is very convenient for generalized mean spherical approximation (GMSA), widely used in calculating properties of polar fluids [9]. In GMSA method Eq. (2) is viewed as form of  $c(r)$  with parameters  $K$  and  $z'$  which are not directly connected to  $\epsilon$  and  $z$ , but are determined through thermodynamic consistency on various routes.

Recently, Henderson et al. [10] (HWLB) published Monte Carlo results for the equation of state for Yukawa fluid with  $z = 1.8$  and compared it with various approximation theories (including the perturbation theory). They concluded that perturbation works well for that system while MSA results are less satisfactory. However, the modifications of MSA (EXP and GMSA) give good results. As it will be demonstrated in this paper variational theory applied for Yukawa potential with a hard-core will produce an analytical equation of state. This equation of state can be utilized for thermodynamic calculations by the use of only a desk calculator.

## 2. Variational method for negative Yukawa potential

According to Mansoori and Canfield [11] the Gibbs-Bogoliubov inequality will be in the following form for the negative Yukawa potential with the hard-sphere fluid as the reference system

$$\frac{A}{NkT} \leq \frac{A_0}{NkT} + 2\pi\rho\beta \int_d^\infty r^2 g_0(r) \frac{-\epsilon e^{-z(r-\sigma)/\sigma}}{r/\sigma}; \quad (4)$$

where  $A_0$ ,  $g_0(r)$  denote the exact Helmholtz free energy and radial distribution function, respectively, for the hard-sphere reference system of diameter  $d$ , and  $\rho$  is the number density of Yukawa system. Here  $d$  is variational parameter, with the understanding that only ratio  $c = d/\sigma \geq 1$  would be physically acceptable. Upon the introduction of dimensionless variables  $x = r/d$ ,  $\rho^* = \rho\sigma^3$ ,  $\eta = \pi\rho d^3/6 = \pi\rho^*c^3/6$ ,  $T^* = kT/\epsilon$  we get

$$\frac{A}{NkT} \leq \frac{A_0}{NkT} - \frac{2\pi}{T^*} \rho^* e^z c^2 \int_1^\infty e^{-zcx} x g_0(x) dx. \quad (5)$$

A necessary requirement of variational as well as perturbation theories is the correct knowledge of the hard-sphere system. The best accessible equation for the Helmholtz free

energy is the Carnahan–Starling [12] formula

$$\frac{A_0}{NkT} = \frac{\eta(4-3\eta)}{(1-\eta)^2} + \frac{A_{id}}{NkT}, \quad (6)$$

where  $A_{id}$  is the free energy of an ideal gas. For the hard-sphere radial distribution function, analytic solution of Percus–Yevick equation due to Wertheim [14] and Thiele [15],  $g_{WT}(r)$ , and its improved Verlet–Weis [13] version,  $g_{VW}(r)$  are exploited. In the case when simpler but less correct  $g_{WT}(r)$  is used, the integral in formula (5) appears to be nothing but  $G(xc)$ , where  $G(s)$  is Laplace transform of  $g_{WT}(r)$

$$G(s) = \int_1^{\infty} e^{-sx} g_{WT}(x) dx. \quad (7)$$

According to Wertheim [14]

$$G(s) = sL(s)/12\eta[L(s) + S(s)e^s], \quad (8)$$

where

$$L(s) = 12\eta[(1 + \frac{1}{2}\eta)s + (1 + 2\eta)] \quad (9)$$

and

$$S(s) = (1-\eta)^2 s^3 + 6\eta(1-\eta)s^2 + 18\eta^2 s - 12\eta(1+2\eta). \quad (10)$$

Therefore by setting Eqs. (6) and (7) in Eq. (5) we get

$$\frac{A}{NkT} \leq \frac{\eta(4-3\eta)}{(1-\eta)^2} - \frac{2\pi}{T^*} \rho^* e^z c^2 G(zc). \quad (11)$$

More accurate results are expected to be obtained when  $g_0(r) = g_{VW}(r)$  is used in Eq. (4),  $g_{VW}(r)$  given by [13]

$$g_{VW}(r/d, \eta) = g_{WT}(r/d_w, \eta_w) + \delta g_1(r), \quad (12)$$

with

$$\delta g_1(r) = \frac{A}{r} e^{-\mu(r-d)} \cos \mu(r-d), \quad (13)$$

$$\eta_w = \eta - \eta^2/16, \quad (14a)$$

$$d_w^3/\eta_w = d^3/\eta, \quad (14b)$$

and

$$\frac{A}{d} = \frac{3}{4} \eta_w^2 \frac{(1 - 0.7117\eta_w - 0.114\eta_w^2)}{(1 - \eta_w)^4}, \quad (15a)$$

$$\mu d = \frac{24A/d}{\eta_w g_{WT}(1, \eta_w)}. \quad (15b)$$

Integral involving  $\delta g_1(r)$  is elementary, i.e.

$$\int_d^\infty \delta g_1(r) r^2 \frac{e^{-z(r-\sigma)/\sigma}}{r/\sigma} dr = \frac{d^3}{c} \frac{A}{d} e^{z(1-c)} \frac{\mu d + zc}{(\mu d + zc)^2 + (\mu d)^2}, \quad (16)$$

whereas, after introducing

$$c_w = \frac{d_w}{\sigma} = \frac{d_w}{d} c, \quad (17)$$

and the following manipulations

$$\int_d^\infty g_{WT}(r/d_w, \eta_w) \frac{e^{-z(r-\sigma)/\sigma}}{r/\sigma} = e^z c_w^2 \left[ G(zc_w, \eta_w) - \int_1^{d/d_w} x g_{WT}(x, \eta_w) e^{-zc_w x} dx \right], \quad (18)$$

no matter whether  $d_w > \sigma$  or not (however,  $d \geq \sigma$ ). Since  $d/d_w$  is nearly equal to 1 ( $d/d_w - 1 = 0.01$  at most) we may expand  $g_{WT}(x, \eta)$  around 1 and use the fact that  $g_{WT}(x)$  and its derivatives can be obtained using continuity of  $g_{WT}(x, \eta) - c_{WT}(x, \eta)$  and its three derivatives (the same procedure was applied by VW [13]). The direct correlation function,  $c_{WT}(x)$ , for  $x < 1$  is given by

$$c_{WT}(x) = -\lambda_1 - 6\eta_w \lambda_2 x - \frac{1}{2} \eta_w \lambda_1 x^3, \quad (19)$$

where

$$\lambda_1 = (1 + 2\eta_w)^2 / (1 - \eta_w)^4, \quad (20a)$$

$$\lambda_2 = -(1 + \frac{1}{2} \eta_w)^2 / (1 - \eta_w)^4. \quad (20b)$$

After a little labor

$$\int_1^{d/d_w} x g_{WT}(x) e^{-zc_w x} dx = e^{-zc_w} \sum_{i=0}^3 B_i \frac{(d/d_w - 1)^{i+1}}{i+1}, \quad (21)$$

where

$$B_0 = \tilde{B}_0 = g_{WT}(1, \eta_w) = \frac{1 + \frac{1}{2} \eta_w}{(1 - \eta_w)^2}, \quad (22a)$$

$$B_{i \geq 1} = \tilde{B}_i + \tilde{B}_{i-1} (1 - zc_w) + \tilde{B}_{i-2} \left[ -zc_w + \frac{(zc_w)^2}{2} \right] (\delta_{i3} + \delta_{i4}) \\ + \tilde{B}_0 \left[ \frac{(zc_w)^2}{2} - \frac{(zc_w)^3}{6} \right] \delta_{i4}, \quad (22b)$$

$$\tilde{B}_1 = 6\eta_w \lambda_2 + \frac{3}{2} \eta_w \lambda_1, \quad \tilde{B}_2 = \frac{6\eta_w \lambda_1}{2!}, \quad \tilde{B}_3 = \frac{6\eta_w \lambda_1}{3!}, \quad (23)$$

( $\delta_{ij}$  denotes here the Kronecker delta). Eventually, free energy calculated with the use of  $g_{vw}(r)$  becomes

$$\frac{A}{NkT} \leq \frac{\eta(3-4\eta)}{(1-\eta)^2} + \frac{1}{T^*} \frac{A_1}{NkT}, \quad \frac{A_1}{NkT} = \sum_{j=1}^3 \frac{A_1^j}{NkT}, \quad (24)$$

where

$$\frac{A_1^0}{NkT} = -2\pi q^* e^z c_w^2 G(zc_w, \eta_w), \quad (25)$$

$$\frac{A_1^1}{NkT} = 2\pi q^* e^{z(1-c_w)} c_w^2 \sum_{i=0}^3 B_i \frac{(d/d_w - 1)^{i+1}}{i+1}, \quad (26)$$

$$\frac{A_1^2}{NkT} = -2\pi q^* e^{z(1-c)} c^2 \frac{A}{d} \frac{\mu d + zc}{(\mu d + zc)^2 + (\mu d)^2}. \quad (27)$$

### 3. Numerical results

Minimization of the right hand side of the variational inequality (4) for the Helmholtz free energy with respect to  $c$  gives  $d = \sigma$  ( $c = 1$ ), which is independent of temperature and density. This value of  $d$  (not equivalent to a minimum of  $A$  in the strict sense) is the lowest physically acceptable, because of  $d < \sigma$  there exists the range  $d < r < \sigma$  in which the perturbation potential becomes infinite. As a result, for  $d = \sigma$  calculations reduce to taking into account the first order in  $1/T$  Zwanzig [16] expansion

$$\frac{A}{NkT} = \frac{A_0}{NkT} + \beta \varepsilon \frac{A_1}{NkT} + \dots \quad (28)$$

With this conclusion Eqs. (11) and (24) become extremely simple and as we will see the results are almost the same as those achieved by more sophisticated methods. The results of the calculations based on Eqs. (11) and (24) are compared with Monte Carlo data and other approximation schemes recently published by HWLB [10]. The free energy values with  $z = 1.8$  are presented in Table I, where Var (WT) and Var (VW) denote free energies calculated from Eqs. (11) and (24), respectively. It is seen that both Var (WT) and Var (VW) give values very similar to those obtained by other methods including the second order perturbation theory [10] using computer data for  $\langle N_i \rangle$  and  $\langle N_i N_j \rangle$ . This is because  $A_2/NkT$  (which is negative), the second order term in Zwanzig expansion, is very small for Yukawa with  $z = 1.8$ , as was calculated by HWLB. According to them it is in absolute value at most 0.07 (at  $q^* = 0.2$ ) comparing to  $\sim 0.3$  for square well and Lennard-Jones fluid (see Figs. 2 and 10 of Henderson and Barker [17] review article). For high densities the variational equation, equivalent to the first order perturbation theory for  $d = \sigma$ , gives the free energy values, which are smaller than the HLWB second order perturbation theory results, although  $A_2/NkT$  is negative. This result is due to inaccuracies in the hard sphere

TABLE I

Comparison of variational calculations of  $A/NkT$  for the Yukawa fluid ( $z = 1.8$ ) (ideal gas terms not included) with the results of other theories calculated by BWLB [10]

$\rho^*$	$T^*$	Pert	MSA	EXP	Var(VW)	Var(WT)
0.4	$\infty$	1.130	1.130	1.130	1.130	1.130
	2.00	-1.132	-1.139	-0.151	-0.129	-0.127
	1.50	-0.559	-0.569	-0.590	-0.549	-0.545
	1.00	-1.422	-1.443	-1.493	-1.389	-1.383
0.6	$\infty$	2.042	2.042	2.042	2.042	2.042
	2.00	0.048	0.039	0.025	0.040	0.045
	1.50	-0.620	-0.631	-0.654	-0.627	-0.621
	1.00	-1.962	-1.976	-2.027	-1.962	-1.953
0.8	$\infty$	3.403	3.403	3.403	3.403	3.403
	2.00	0.613	0.600	0.588	0.597	0.602
	1.50	-0.318	-0.334	-0.355	-0.338	-0.332
	1.00	-2.183	-2.206	-2.247	-2.209	-2.199
	0.70	-4.586	-4.164	-4.695	-4.614	-4.600

TABLE II

Comparison of variational calculations of  $PV/NkT$  for Yukawa fluid ( $z = 1.8$ ) with the results of Monte Carlo and other theories calculated by BWLB [10]

$\rho^*$	$T^*$	MC	Pert	MSA		GMSA <sup>b</sup>	Var(VW)	Var(WT)
				$E^a$	$P^b$			
0.4	$\infty$	2.52	2.518	2.518	2.481	2.518	2.518	2.518
	2.00	1.08	1.123	1.122	0.943	1.122	1.100	1.104
	1.50	0.69	0.664	0.666	0.422	0.655	0.627	0.627
	1.00	-0.21	-0.246	-0.229	0.645		-0.318	-0.318
0.6	$\infty$	4.22	4.283	4.283	4.091	4.283	4.283	4.283
	2.00	2.04	1.985	1.978	1.594	1.992	1.958	1.962
	1.50	1.21	1.226	1.219	0.760	1.235	1.183	1.188
	1.00	-0.27	-0.281	-0.283	-0.911	-0.288	-0.367	-0.360
0.8	$\infty$	7.65	7.750	7.750	7.001	7.750	7.750	7.750
	2.00	4.27	4.459	4.433	3.476	4.464	4.425	4.424
	1.50	3.31	3.368	3.332	2.301	3.373	3.318	3.316
	1.00	1.29	1.195	1.137	0.049	1.198	1.102	1.099
	0.70	-1.63	-1.582	-1.668	-3.072	-1.594	-1.747	-1.751

<sup>a</sup> Calculated from energy equation. <sup>b</sup> Calculated from pressure equation.

radial distribution functions which we have used and probably also due to some inaccuracy in the Monte Carlo data [19] exploited in the HWLB calculations. For example, as was previously pointed out by Madden and Fitts [18], Verlet-Weis parametrization of  $g_o(r)$ ,

based on unpublished Verlet-Schiff simulation, [13], predicts  $g_0(d)$ , which differs by 0.06 for  $\rho = 0.8$  from extensive Monte Carlo simulation of Barker and Henderson [19].

It should be also mentioned that the difference between the free energies Var (WT) and Var (VW) values is very small (e.g. of 0.015 for  $\rho = 0.8$ ). Similarly, taking into account only  $B_0$  and  $B_1$  terms in Eq. (21) instead of four terms makes difference of at most  $10^{-4}$ .

Having the Helmholtz free energy, pressure can be calculated through numerical differentiation. The variational results as presented in Table II are slightly inferior to the results of other theories. Next, because of very simple temperature dependence of the first order perturbation free energy, the configurational entropy and the internal energy can be easily obtained as:

$$\frac{S}{Nk} = -\frac{\beta A_0}{N}, \quad (29)$$

$$\frac{U}{N\epsilon} = \frac{A_1}{NkT}, \quad (30)$$

TABLE III

Values of  $U/N\epsilon$  for the Yukawa fluid ( $z = 1.8$ )

	$T^*$	MC	Pert	MSA	GMSA	Var(VW)	Var(WT)
0.4	$\infty$	-2.495	-2.495	-2.513	-2.495	-2.518	-2.513
	2.00	-2.583	-2.552	-2.568	-2.595	-2.518	-2.513
	1.50	-2.622	-2.572	-2.594	-2.658	-2.518	-2.513
	1.00	-2.832	-2.610	-2.665		-2.518	-2.513
0.6	$\infty$	-3.975	-3.975	-3.995	-3.975	-4.004	-3.995
	2.00	-4.030	-4.006	-4.017	-4.031	-4.004	-3.995
	1.50	-4.051	-4.017	-4.026	-4.056	-4.004	-3.995
	1.00	-4.073	-4.039	-4.050	-4.145	-4.004	-3.995
0.8	$\infty$	-5.573	-5.573	-5.602	-5.573	-5.612	-5.602
	2.00	-5.622	-5.589	-5.608	-5.598	-5.612	-5.602
	1.50	-5.630	-5.594	-5.611	-5.607	-5.612	-5.602
	1.00	-5.635	-5.605	-5.616	-5.529	-5.612	-5.602
	0.70	-5.658	-5.619	-5.624	-5.672	-5.612	-5.602

with  $A_1$  defined by Eq. (28).  $S$  and  $U$  as given by Eqs. (29) and (30) are temperature independent which is not satisfactory. However, it should be mentioned that for the Yukawa fluid the internal energy is very weak function of temperature as presented by the HWLB Monte Carlo calculations and the results of the other theories in Table III.

#### 4. Conclusions

It is shown that for the Yukawa fluid, through the variational method it is possible to obtain thermodynamic quantities in analytic forms. This is because for one Yukawa tail minimization of the right-hand side of the variational inequality for the Helmholtz free

energy gives  $d = \sigma$ , which is independent of temperature and density. As a result, thermodynamic properties can then be calculated with the effort incurred not very much greater than for the case of hard-sphere system.

Although the intermolecular Yukawa potential is a simple potential model for some values of  $z$  and  $\epsilon$  of this model qualitative calculations can be made for real fluids. However, with the use of two Yukawa functions (one negative and one positive) one can construct potentials functions in more realistic forms resembling the true pair potentials. Having this in mind variational method offers promising possibilities because it can be very easily generalized to the case of linear combination of Yukawa functions with the same  $\sigma$  or for mixtures of Yukawa functions with hard-cores of additive diameters. We have found that for two Yukawa functions there exists a minimum for the right hand side of inequality (4) for a wide range of potential and thermodynamic parameters. The variational parameter  $c$  (Eq. (5)) is then temperature dependent, this remedying the deficiencies of the one Yukawa case. Minimization in the case of two Yukawa potential is not difficult because the free energy is in analytic form. The results obtained should then be comparable in accuracy to the results of the other successful theories of liquids.

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