

EQUATION OF STATE OF A HARD CORE FLUID WITH A TWO-YUKAWA TAIL: TOWARD A SIMPLE ANALYTIC THEORY*

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Thermodynamic properties of simple fluids are calculated using variational theory for a system of hard-core potential with a two-Yukawa tail. Likewise one Yukawa-tail case (C. Jędrzejek, G. A. Mansoori, *Acta Phys. Pol.* A56, 583 (1979)) the working formulas are analytic. Five parameters of the two Yukawa system are chosen so as to get the best fit to a real argon potential or an "argon-like" Lennard-Jones potential. The results are fairly good in light of the extreme simplicity of the method. The discrepancies result from using the variational method and a different shape of Yukawa type potential in comparison to the real argon and L-J potentials.

1 Introduction

Equilibrium properties of simple liquids are now very well understood [2]. Therefore, the focus of interest is now concentrated on more complicated liquid substances; nonspherical liquids, polar and ionic liquids, and liquid mixtures. Most methods, however, even in the simple liquids are complicated. For example some of them, as Barker-Henderson perturbation method [2] use directly Monte Carlo data for hard-sphere reference systems. Thus, there is still room for simplifications because some achievements in the simple liquid theory can hopefully be used in calculations of the properties of more complex liquid substances.

One hope in this respect is the use of Yukawa type potentials

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

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where $x = r/\sigma$, and σ is the diameter of the hard-core of the molecules. Properties of liquids interacting through Yukawa type potentials have been widely investigated. There exist analytic solutions for direct correlation function for this potential in so called mean-spherical approximation for single Yukawa [3], generalized later for arbitrary number of Yukawa functions [4], and for mixture of Yukawa fluids [5].

Yukawa potential is also of interest in liquid metal theory and it appears when certain approximations are made on the dielectric function $\epsilon(k)$. Firey and Ashcroft [6] used the variational theory for calculation of thermodynamic properties of mixture of ions interacting via a screened Coulomb potential in a Yukawa form.

Further understanding of Yukawa system properties is due to Henderson et al. [7] who performed the Monte Carlo computations of thermodynamic properties for one Yukawa potential fluid with $z = 1.8$ and compared them with many theoretical approximation methods.

Recently, we applied the variational method [1], which gives most formulae for thermodynamic properties in analytic form, to single negative Yukawa potential with $z = 1.8$ (henceforth this work will be referred to as I). For this potential the variational method was equivalent to the first order Zwanzig perturbation theory [8], because variational parameter, the diameter of hard cores of Yukawa system, was independent of the temperature and the density.

The aim of the present paper is to apply the previously developed method to the system with the potential consisting of a hard-core with two Yukawa tails, one positive and the other negative definite. In this case it is possible to construct potential functions in realistic forms resembling the true pair potentials. The two Yukawa function potential has five coefficients which can be used to fit a realistic potential. In this work we investigate various methods of the fitting to the real argon potential with the understanding that they can further be used for other substances. Moreover, although two functions Yukawa potential has five free parameters, its shape has somewhat different nature than for example Barker-Fisher-Watts (BFW) potential proven to be the closest approximate potential to real argon one. Nevertheless we feel that extreme simplicity due to the form of Yukawa potential and the use of variational method in enough compensation for some lack in accuracy, particularly for mixtures. Therefore, we report also the formulae for the variational method with Yukawa potential for mixtures.

2. Variational method for two Yukawa potentials

A. One component case

According to Mansoori and Canfield [9] the variational Gibbs-Bogoliubov inequality will be in the following form for two Yukawa functions potential with the hard-sphere fluid as the reference system

$$\frac{A}{NkT} \leq \frac{A_0}{NkT} + 2\pi\rho\beta \int_d^\infty dr r^2 g_0(r) \left[\frac{-\epsilon_1 e^{-z_1 \left(\frac{r-\sigma}{\sigma}\right)} + \epsilon_2 e^{-z_2 \left(\frac{r-\sigma}{\sigma}\right)}}{\frac{r}{\sigma}} \right]. \quad (2)$$

In this formula $A_0, g_0(r)$ denote the exact Helmholtz free energy and radial distribution function, respectively, for the hard-sphere reference system of diameter d and ρ is the number density of Yukawa system. The right hand side of inequality (2) is minimized with respect to d , while $\varepsilon_1, \varepsilon_2, z_1, z_2, \sigma$ are assumed to be known. Upon the introduction of the dimensionless variables $x = r/d, c = d/\sigma, \rho^* = \rho\sigma^3, \eta = \pi\rho d^3/6 = \pi\rho^*c^3/6$ one obtains

$$\frac{A}{NkT} \leq \frac{A_0}{NkT} + \frac{2\pi}{kT} \rho^* \sum_{i=1}^2 (-1)^i \varepsilon_i e^{z_i} \int_1^{\infty} dx e^{-z_i c x} x g_{HS}(x). \quad (3)$$

Next we proceed in a completely analogous way as in I, i.e. using property that

$$G(x) = \int_1^{\infty} dx e^{-sx} x g_{PY}(x; \eta) \quad (4)$$

is a known Laplace transform of PY solution for radial distribution function of hard-sphere system (multiplied by x) [10]. After using the Carnahan-Starling [11] formula for A_0 and Verlet-Weis modification of $g_{HS}(r)$ [12] we get

$$\frac{A}{NkT} \leq \frac{\eta(3-4\eta)}{(1-\eta)^2} + \sum_{i=1}^2 (-1)^i \frac{\varepsilon_i}{kT} \frac{A_{1i}}{NkT}, \quad (5)$$

where

$$\frac{A_{1i}}{NkT} = \sum_{j=1}^3 \frac{A_{1i}^{(j)}}{NkT} \quad (6)$$

and

$$\frac{A_{1i}^{(0)}}{NkT} = -2\pi\rho^* e^{z_i} c_w^2 G(z_i c_w, \eta_w), \quad (7)$$

$$\frac{A_{1i}^{(1)}}{NkT} = 2\eta\rho^* e^{z_i(1-c_w)} c_w^2 \sum_{k=0}^3 B_{ki} \frac{(d/d_w - 1)^{k+1}}{k+1} \quad (8)$$

$$\frac{A_{1i}^{(2)}}{NkT} = -2\pi\rho^* e^{z_i(1-c)} c^2 \frac{A}{d} \frac{\mu d + z_i c}{(\mu d + z_i c)^2 + (\mu d)^2}. \quad (9)$$

Here $B_{ki} = B_{ki}(\eta, c, z_i)$ and their form can be found in I. When the $g_{PY}(r)$ is used as the hard-sphere reference system radial distribution function $A_{1i}^{(1)} = A_{1i}^{(2)} = 0$ and the form of $A_{1i}^{(0)}$ is simpler because $G(s; \eta)$ depends on actual η , and not on η_w as in the modified Verlet-Weis $g_{VW}(r)$ case.

B. The variational method for mixtures

Two Yukawa potential for a mixture is in the following form

$$u_{ij}(r) = \begin{cases} \infty, & r < \sigma_{ij} \\ \frac{A_{ij}}{r} e^{-B_{ij}r} - \frac{C_{ij}}{r} e^{-D_{ij}r}, & r > \sigma_{ij} \end{cases} \quad (10)$$

where in denotations used in Eq. (1) $A_{ij} = \varepsilon_{ij}^{(2)} \exp(z_{ij}^{(2)})$, $C_{ij} = \varepsilon_{ij}^{(1)} \exp(z_{ij}^{(1)})$.

Accordingly, the variational inequality takes the form

$$\frac{A}{NkT} \leq \frac{A_0}{NkT} + 2\pi\varrho\beta \sum_{ij} x_i x_j \int_{d_{ij}}^{\infty} dr r g_{ij}^{\text{HS}}(r) (A_{ij} e^{-B_{ij}r} - C_{ij} e^{-D_{ij}r}), \quad (11)$$

where x_{ij} stand for concentrations of the components and A_0 can be obtained from the Mansoori et al. equation of state [13]. Such form is convenient because appearance of repulsive Yukawa function makes the values of σ_{ij} not matter in the variational method, if they are enough small — they only set up a scale. After some manipulations with the use of Lebowitz solution of the Percus–Yevick equation for mixtures of hard-spheres with additive diameters [14]

$$\frac{A}{NkT} \leq \frac{A_0}{NkT} + 12\beta \sum (x_i x_j)^{1/2} [A_{ij} H_{ij}(B_{ij}; \{\eta\}) - C_{ij} H_{ij}(D_{ij}; \{\eta\})], \quad (12)$$

where for the explicit form of $H_{ij}(s)$ function, which are available in an analytic form

$$H_{ij}(s) = H_{ji}(s) = (\gamma_i \gamma_j)^{1/2} \int_d^{\infty} dr r g_{ij}(r) \exp(-sr) \quad (13)$$

we refer to the Lebowitz paper [14] $\left(\gamma_i = \frac{\pi}{6} \sigma x_i\right)$.

The minimization of the rhs of the inequality (12) is with respect to d_{ij} (or in dimensionless units: $c_{ij} = d_{ij}/\sigma_{ij}$). All c_{ii} and $c_{ij} = c_{ji}$, $i \neq j$, are independent even if the unlike pair interaction parameters are assumed according to the rule similar to the Lorentz–Berthelot one [15]

$$A_{ij} = (A_{ii} \cdot A_{jj})^{1/2}, \quad C_{ij} = (C_{ii} \cdot C_{jj})^{1/2},$$

$$\frac{1}{B_{ij}} = \left(\frac{1}{B_{ii}} + \frac{1}{B_{jj}}\right)^{1/2}, \quad \frac{1}{D_{ij}} = \left(\frac{1}{D_{ii}} + \frac{1}{D_{jj}}\right)^{1/2}.$$

There are also possible more accurate and at the same time more complicated choices, e.g.

$$A_{ij} = (1 - K_{ij}^A) (A_{ii} A_{jj})^{1/2}, \quad C_{ij} = (1 - K_{ij}^C) (C_{ii} C_{jj})^{1/2}.$$

3. Determination of the values of the coefficients for two Yukawa functions

It should be stressed that a Yukawa type potential is not based on strong physical grounds, as Barker et al. (BFW) [16] and Parson et al. [17] potentials. Specifically it decays

in a way different from accepted $\sum_{i=0}^2 C_{6+2i} \frac{1}{r^{6+2i}}$ form. Nevertheless, having five free

parameters at disposal one can expect to get a fit good for practical applications, because a general shape of the potential is compatible with the shapes of real potentials. We expect some lack of accuracy in representing a real potential in the Yukawa form is a small price for a computational convenience.

We checked several methods of fitting the Yukawa potential. A pure fit to second virial coefficient appeared to be completely unsatisfactory because of extreme multi-modality of this optimization. The similar problem has been pointed out in determining the parameters for Lennard-Jones potential from viscosity data by Vogl and Ahlert [8]. Additionally, such optimization is time consuming because the formula for B_2

$$B_2 = 2\pi\tilde{N}\sigma^3 \left(\frac{1}{3} - \int_1^{\infty} \left\{ \exp \left[\frac{\varepsilon_1}{kTx} \exp[-z_1(x-1)] - \frac{\varepsilon_2}{kTx} \exp[-z_2(x-1)] \right] - 1 \right\} x^2 dx \right) \quad (16)$$

is not subjected any simplifications as for example for Lennard-Jones case [19]. Therefore we exploit two other methods: 1) fitting to the second virial coefficient but with the previously determined: r_m — the distance between the atoms at the minimum of the potential, $u(r_m)$ — value of the potential at the minimum, r_0 — the distance between the atoms for which $u(r_0) = 0$, 2) fitting directly to the BFW potential [16].

In the first method we cast the potential (1) to the form of Eq. (10)

$$u(r) = \begin{cases} \infty, & r < \sigma \\ \frac{A}{r} e^{-Br} - \frac{C}{r} e^{-Dr}, & r > \sigma. \end{cases} \quad (17)$$

Using the following conditions: $u(r_0) = 0$, $u(r_m) = \varepsilon$, $\left. \frac{du}{dr} \right|_{r_m} = 0$ the potential can be transformed into

$$u(r) = -\varepsilon \frac{r_m}{r} \frac{E^{\frac{r-r_0}{r_m-r_0}} - 1}{E-1} \exp \left\{ \frac{r-r_m}{r_m} - \frac{E \ln E / (E-1)}{r_m-r_0} (r-r_m) \right\}, \quad r > \sigma, \quad (18)$$

where

$$E = \frac{1+Dr_m}{1+Br_m} < 1 \quad (19)$$

so as the attractive part be more long-ranged than repulsive one. This potential is used to fit the second virial coefficient with the two unknown parameters E and σ . Having determined E and σ the coefficients from Eq. (17) are as follows:

$$D = \frac{E \ln E}{E-1} \frac{1}{r_m - r_0} - \frac{1}{r_m}, \quad (20)$$

$$B = \frac{\frac{1 + Dr_m}{E} - 1}{r_m}, \quad (21)$$

$$A = \frac{-\varepsilon r_m}{\exp(-Br_m) - \exp[-r_0(B-D) - Dr_m]}, \quad (22)$$

$$C = A \exp[-r_0(B-D)]. \quad (23)$$

The calculation of $\varepsilon_1, \varepsilon_2, z_1, z_2$ from A, B, C, D is straightforward. In the second method the following expression was minimized:

$$R = \sum_{i=0}^N (u_{\text{BFW}}(r_i) - u_Y(\varepsilon_1, \varepsilon_2, z_1, z_2; r_i))^2 \exp\left[-\left(\frac{r_i - r_m}{p}\right)^2\right], \quad (24)$$

where $r_0 = \sigma$ and $r_N = 4r_m$. The exponential expression in R with the variance p^2 is to account for the importance of the region near minimum in determining potential. This kind of fitting involves more arbitrariness than the previous one because depends on the postulated σ and p . It was found that such an overall fit is not satisfactory, because it cannot properly balance contributions from different r -regions and consequently the obtained B_2 values are not good. Therefore, we present the results only for the first method. The experimental data for B_2 were taken from Byrne et al. [20], Whalley et al. [21], and Michels et al. [22, 23]. All points below 103 K were discarded since there is good evidence (Hanley et al. [24]) that the experimental B_2 are in error in low temperatures. Furthermore, as the potential used has a hard-core it is not possible to account for quantum correction for B_2 , which becomes important in lower temperatures, in a simple way (ordinary h^2 expansion is not valid [25]). Hence, using the data with minimal quantum correction is justified. In all cases we used 33 B_2 experimental points to fitting.

Aside from fitting Yukawa potential to real argon one we did the same fit for Lennard-Jones potential, for which there exist extensive body of computer simulation and different approximation theories data. We chose the values $\varepsilon = 119.8$ K, $\sigma = 3.405$ Å for which L-J potential is a good effective potential for real argon [2]. In Table I we present the values of parameters of Yukawa potential which give the best values of second virial coefficients. In Fig. 1 the shapes of such fitted potentials, $u_Y(r)$ are compared with the shapes of BFW L-J potentials, respectively. In both cases Yukawa potential is steeper,

TABLE I

The parameters obtained through fitting Yukawa potential, Eq. (1), to BFW (real argon) and L-J potentials [2]

	$\frac{\varepsilon_1}{k}$	$\frac{\varepsilon_2}{k}$	z_1	z_2	σ	RMS ^a	Number of data
BFW 1	782.95	6170.7	2.6558	11.1180	2.7018	0.8	33
BFW 2	1332.20	36073.0	2.2628	9.5376	2.3121	1.0	33
L-J ($\varepsilon = 119.8$ K, $\sigma = 3.405$ Å)	468.74	4090.5	2.1786	12.1720	2.7988	1.6	33

$${}^a \text{RMS} = \sqrt{\frac{1}{N} \sum_{i=1}^N (B_2^{\text{exp}} - B_2^{\text{fit}})^2}$$

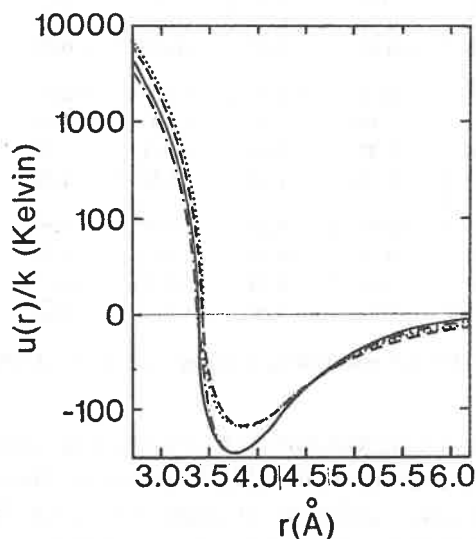


Fig. 1. The pair energy $u(r)$ for argon: --- BFW potential [16]; solid curve, $u_Y(r)$ fitted to $u_{\text{BFW}}(r)$ according to Eqs. (18); dashed line, L-J potential ($\varepsilon = 119.8$ K, $\sigma = 3.405$ Å); , $u_Y(r)$ fitted to L-J potential

for $r_0 < r < r_m$ goes outside and falls off faster in comparison with the corresponding BFW or L-J potential. The differences between a and b versions of $u_Y(r)$ from Table I fitted to $U_{\text{BFW}}(r)$ are not distinguishable in the scale of Fig. 1.

4. Numerical results

In order to check out the sensitivity of thermodynamic properties on the shape of the potential we first calculated the Helmholtz free energy and the pressure through variational method using two Yukawa functions potential, $u_Y(r)$ fitted to $u_{L-J}(r)$. These results were

TABLE II

Values of $A/Nk_B T$ for 6-12 potential

$k_B T/\epsilon$	$\rho\sigma^3$	Simul. ^a	BH1	BH2	Var. (PY)	Var. (VW)	Yukawa Pot. Var. (PY)	Yukawa Pot. Var. (VW)
2.74	0.60	-0.34	-0.31	-0.33	-0.19	-0.18	-0.19	-0.18
	0.70	+0.01	+0.02	+0.01	+0.20	+0.21	0.19	0.21
	0.80	0.43	0.46	0.42	0.65	0.69	0.65	0.69
	0.90	0.93	0.99	0.95	1.21	1.27	1.22	1.28
	1.00	1.59	1.66	1.62	1.92	2.01	1.93	2.02
1.35	0.60	-1.77	-1.65	-1.75	-1.59	-1.57	-1.60	-1.59
	0.70	-1.65	-1.51	-1.63	-1.42	-1.39	-1.43	-1.60
	0.80	-1.41	-1.26	-1.41	-1.13	-1.07	-1.14	-1.04
	0.90	-1.02	-0.84	-1.01	-0.67	-0.57	-0.68	-0.58
	0.95	-0.72	-0.55	-0.72	-0.35	-0.23	-0.36	-0.24
1.15	0.60	-2.99	-2.15	-2.30	-2.10	-2.09	-2.12	-2.11
	0.70	-2.25	-2.10	-2.26	-2.02	-1.99	-2.04	-2.01
	0.80	-2.06	-1.92	-2.10	-1.81	-1.74	-1.82	-1.76
	0.90	-1.79	-1.56	-1.76	-1.40	-1.29	-1.41	-1.31
0.75	0.60	-4.24	-3.99	-4.29	-4.01	-3.99	-4.05	-4.03
	0.70	-4.53	-4.26	-4.28	-4.24	-4.24	-4.31	-4.27
	0.80	-4.69	-4.37	-4.74	-4.38	-4.30	-4.40	-4.32
	0.90		-4.26	-4.67	-4.22	-4.08	-4.23	-4.09

^a Verlet and Levesque (1967), Verlet (1967), Levesque and Verlet (1969), Hansen and Verlet (1969).

compared with the variational calculations for Lennard-Jones potential, other approximation theories results and Monte Carlo data [2]. From the results of Tables II and III it can be seen that despite the certain difference in shape, $u_Y(r)$ gives almost the same values of free energy and pressure as corresponding u_{L-J} potential, if the variational theory is used. This indicates that two Yukawa functions potential can be useful as model potential in calculations of thermodynamic properties, provided its parameters are appropriately chosen. That the variational theory give worse results than perturbation theories, when a potential with hard core is used as reference potential, is due to the fact that the shape of the potential for $r < d$ has no meaning in the variational method, while in the other methods it serves for the determination of the most appropriate d . The results are worse, when improved Verlet-Weis $g_{VW}(r)$ is used instead of $g_{PY}(r)$.

TABLE III

Values of $pV/Nk_B T$ for 6-12 potential

$k_B T/\epsilon$	$\rho\sigma^3$	Simul. ^a	Simul. ^b	BH1	BH2	Var. (PY)	Var. (VW)	Yukawa Pot.	
								Var. (PY)	Var. (VW)
2.74	0.65	2.22		2.24	2.22	2.48	2.54	2.49	2.56
	0.75	3.05		3.14	3.10	3.33	3.54	3.45	3.57
	0.85	4.38		4.48	4.44	4.79	4.98	4.83	5.02
	0.95	6.15		6.41	6.40	6.69	6.97	6.76	7.04
1.35	0.10	0.72		0.77	0.74	0.78	0.78	0.77	0.77
	0.20	0.50		0.55	0.52	0.56	0.56	0.55	0.55
	0.30	0.35		0.39	0.36	0.39	0.39	0.38	0.38
	0.40	0.27		0.26	0.26	0.31	0.32	0.30	0.31
	0.50	0.30		0.31	0.27	0.39	0.43	0.39	0.42
	0.55	0.41		0.43	0.35	0.53	0.58	0.53	0.58
	0.65	0.80		0.91	0.74	1.08	1.19	1.09	1.20
	0.75	1.73		1.87	1.64	2.14	2.34	2.16	2.36
	0.85	3.37		3.54	3.36	3.92	4.24	3.95	4.27
0.95	6.32		6.21	6.32	6.67	7.16	6.72	7.20	
1.00	0.65	-0.25		-0.21	-0.36	-0.10	+0.04	-0.08	0.05
	0.75	+0.58	0.48	+0.71	+0.53	+0.95	1.20	0.98	1.22
	0.85	2.27	2.23	2.48	2.25	2.90	3.32	2.94	3.35
	0.90	~3.50		3.79	3.53	4.34	4.84	4.39	4.88
0.72	0.85	0.40	0.25	0.70	0.25	1.05	1.59	1.11	1.62
	0.90		~1.60	2.15	1.63	2.73	3.39	2.77	3.41

^a Verlet and Levesque (1967), Verlet (1967), Levesque and Verlet (1969).^b McDonald and Singer (1969).

Next, we calculated the internal energy and pressure for real argon using two different Yukawa potentials, with parameters given in Table I, fitted to BFW potential [16] to make calculations which are directly comparable with experimental results three-body interactions together with a pair potential have to be included. Therefore, we minimized

$$\frac{A}{NkT} \leq \frac{A_0}{NkT} + \frac{2\pi\rho}{kT} \int_d^\infty dr r g_{HS}(r) u_Y(r) + \frac{A_{3b}}{NkT}, \quad (25)$$

where $\frac{A_{3b}}{NkT}$ has the following analytic form derived by Barker et al. (see [26]) through Pade approximation

$$\frac{A_{3b}}{NkT} = \frac{v\eta^2}{kTd^3} \frac{0.87748 + 11.76739\eta - 4.20027\eta^2}{1 - 1.12789\eta + 0.73166\eta^2}. \quad (26)$$

TABLE IV
Calculated (variational method for Yukawa potential), experimental and BH2 [2] internal energies for fluid argon

V (cm ³ /mole)	T K	U_{cal}				U (BH2)	U_{exp} (cal/mole)
		Var. (PY)		Var. (VW)			
		a	b	a	b		
Fluid on melting line							
23.66	180.15	-1277	-1281	-1243	-1247	-1297	
22.96	197.78	-1271	-1221	-1176	-1181	-1235	
23.10	201.32	-1210	-1214	-1171	-1175	-1236	
21.31	273.11	-899	-903	-839	-844	-940	
21.09	273.11	-875	-880	-813	-818	-924	
20.46	323.14	-637	-642	-564	-569	-664	
Fluid							
27.04	100.00	-1411	-1414	-1396	-1400	-1423	-1432
29.66	100.00	-1303	-1306	-1299	-1298	-1313	-1324
30.65	140.00	-1198	-1200	-1190	-1193	-1213	-1209
39.36	140.00	-1042	-1044	-1039	-1042	-1061	-1069
41.79	140.00	-869	-871	-870	-872	-906	-922
48.39	150.87	-731	-734	-733	-735	-784	-789
57.46	150.87	-603	-604	-604	-606	-679	-689
70.73	150.87	-477	-478	-478	-480	-573	-591
91.94	150.87	-356	-357	-357	-358	-462	-481

TABLE V
Calculated (variational method for Yukawa potential), experimental and BH2 [2] pressures for fluid argon

V (cm ³ /mole)	T K	$P_{cal}(\text{bar})$				P (BH2)	P_{exp} (bar)
		Var. (PY)		Var. (VW)			
		a	b	a	b		
Fluid on melting line							
23.66	180.15	5570	5565	5920	5915	4907	4999
22.96	197.78	7110	7105	7520	7514	6319	6140
23.10	201.32	6993	6988	7393	7388	6143	6335
21.31	273.11	13159	13150	13765	13762	11645	11380
21.09	273.11	13821	13817	14461	14458	12585	
20.46	323.14	17743	17742	18500	18500	15513	15354
Fluid							
27.04	100.00	886	881	1051	1046	655	661
29.66	100.00	241	238	395	342	118	106
30.65	140.00	779	775	874	870	588	591
39.36	140.00	259	256	303	300	470	480
41.79	140.00	50	48	67	65	18	37
48.39	150.87	60	58	67	65	54	62
57.46	150.87	43	41	44	43	58	51
70.73	150.87	47	46	47	46	50	50
91.94	150.87	54	54	54	54	50	50

TABLE VI

Contribution to the internal energy of argon calculated through the variational method for Yukawa potential, Var. (PY)

V (cm ³ /mole)	T	$U(2b)$		U		$U(2b)$ (BH2)	U (BH2)	U_{exp} (cal/mole)
		a	b	a	b			
27.04	100.00	-1489	-1493	-1411	-1413	-1525	-1423	-1432
29.66	100.00	-1364	-1367	-1303	-1306	-1394	-1313	-1329
30.65	100.00	-1278	-1281	-1198	-1200	-1285	-1213	-1209
41.79	140.00	- 895	- 898	- 869	- 871	- 951	- 906	- 922
70.73	150.87	- 484	- 486	- 477	- 478	- 604	- 573	- 591

TABLE VII

Contribution to the pressure of argon calculated through the variational method for Yukawa potential, Var. (PY)

V (cm ³ /mole)	T K	$p(2b)$		p		$p(2b)$ (BH2)	p (BH2)	p_{exp} (atm)
		a	b	a	b			
27.04	100.00	540	535	898	893	240	646	652
29.66	100.00	2	-2	244	241	-148	116	105
30.65	140.00	652	648	789	784	+349	580	583
41.79	140.00	-19	-21	51	49	-34	18	37
70.73	150.87	36	35	48	47	+35	49	49

We used for v the value $v = 73.2 \cdot 10^{-109} \text{ J-m}^9$ [26]. Quantum corrections which are small for argon were neglected. In Table IV the internal energy and in Table V the pressure were calculated through variational method are presented and compared with Barker-Henderson BH2 theory results and experimental data. In Tables VI and VII are shown the contributions from two body potential to the internal energy and to the pressure. These results illustrate that generally calculated pressure is higher than experimental one, with $p_{VW} > p_{PY}$. There are practically no differences between the results obtained using two different sets of Yukawa potential parameters from Table I.

5. Conclusions

In this paper we calculated the properties of real argon using the two Yukawa function potential. When the variational method is applied for such potential the thermodynamic quantities have analytic forms. The results obtained are worse than the results of very much more effort and time consuming methods (with exception of BH2, which uses functions fitted to Monte Carlo simulation [2]), but not very different from experimental data. The attempt of fitting the Yukawa potential to the potentials of real substances was dictated not only by the needs of variational theory but can be useful for using Yukawa type po-

tentials in other approximation schemes, e.g. MSA or GMSA methods [27]. The most promising application of the presented approach should be for mixtures for which it is known the variational method gives good excess properties [15]. Then the simplicity of the method is a prevailing factor particularly because the procedure of adjusting the $u_{ij}(r)$, $i \neq j$, potential parameters is crucial. This makes the theories without fitted parameters, the theories with fitted parameters. As a result some less satisfactory theories can be brought into agreement with experiment by using a reasonable values of $u_{ij}(r)$ parameters.

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