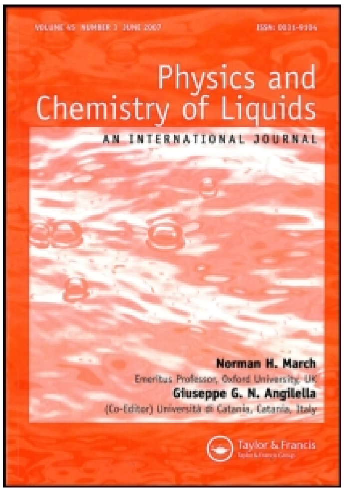

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Performance of the Double Yukawa Potential in the Variational Theory of Simple Liquids

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A variational theory for classical fluids based on a hard-sphere reference system is used to examine the differences between performing the calculations with a Lennard-Jones pair potential or a double Yukawa one, in the range of densities up to four times that of the Argon triple point. Likewise we verify that the results achieved using the Verlet–Weis $g_{VW}(r)$ are quite similar to those obtained with the Percus–Yevick $g_{PY}(r)$.

Key Words: Hard sphere model, Lennard-Jones fluid.

I INTRODUCTION

Recently, Foiles and Ashcroft[1] have shown that a double Yukawa potential (DY), with suitable chosen parameters, provides a good representation of pair potentials of simple classical fluids and, when used in conjunction with the variational theory, leads to reasonable good predictions of their thermodynamic properties (in the low temperature limit). This potential presents the advantage of giving an analytic expression for the Helmholtz free energy. Concerning the choice of the reference system Foiles and Ashcroft have obtained good results by the

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combination of the Percus-Yevick (PY) hard-spheres radial distribution function (RDF) $g_{\mathrm{PY}}(r)$, together with the expression for the hard-spheres entropy as obtained from the PY approximation via the virial equation of state, S_V. With the same DY potential Gonzalez and Silbert (GS) improved the precedent results using a reference system constructed by the combination of the Verlet and Weis[3] semiempirical expression for the hard spheres RDF, together with the entropy obtained from the Carnahan and Starling[4] equation of state, S_{CS} corrected by an empirical term proposed by Ross[5] which accounts for the softness of the repulsive potential. Both works were carried out for the low temperature case.

In this paper we extend the work of GS to high temperatures and also by using a Lennard-Jones potential. The results are compared with the previous ones obtained by Ross.

II FORMALISM AND RESULTS

The variational theory states that the free energy of a classical fluid, F, is given by

$$\frac{\beta F}{N} \leq \frac{\beta \tilde{F}}{N} = \frac{3}{2} + \frac{\beta F_1}{N} - \frac{S_{hs}}{Nk_B} \tag{1}$$

where

$$\beta F_1/N = \tfrac{1}{2}\beta\rho \int g_{hs}(r)\phi(r)\, d\mathbf{r}. \tag{2}$$

k_B is the Boltzmann constant, $\beta = (k_B T)^{-1}$, ρ is the number density, g_{hs} is the RDF and S_{hs} is the entropy of the hard spheres reference system. The spheres are taken to have diameter d and packing fraction $\eta = \frac{1}{6}\pi\rho d^3$. An upper bound on F can then be obtained by minimizing Eq. (1) with respect to η (or d). On the other hand Watabe and Young[6] have shown that the equation of state consistent with the choice of η as a variational parameter, is given by

$$P = \rho K_B T - \tfrac{1}{6}\rho^2 \int r \frac{\partial\phi(r)}{\partial r} g_{hs}(r)\, d\mathbf{r} \tag{3}$$

thus disposing of the need for using numerical derivatives. The excess internal energy (U) is obtained by

$$\beta U = \beta\left(\frac{\partial \beta F}{\partial \beta}\right)_\rho \approx \beta\left(\frac{\partial \beta \tilde{F}}{\partial \beta}\right)_\rho \tag{4}$$

Table 1 Free energy F/Nk_BT as a function of reduced temperature and density. (a) Computer simulation for Lennard-Jones fluid (LJ-Sim[7]). (b) Variational calculations: (i) with $\phi_{LJ}(r)$, $g_{PY}(r)$ and S_{soft}[5]; (ii) with $\phi_{LJ}(r)$, $g_{VW}(r)$ and S_{Soft} (LJ Ross: this work); (iii) with $\phi_{DY}(r)$, $g_{VW}(r)$ and S_{soft} (DY-Ross: this work).

k_BT/ε	$\rho\sigma^3$	LJ-Sim	Ross	LJ-Ross	DY-Ross
100.00	0.2	−2.40	−2.41	−2.41	−2.41
	0.4	−1.47	−1.48	−1.48	−1.48
	0.5	−1.11	−1.13	−1.13	−1.13
	0.666	−0.59	−0.61	−0.61	−0.60
	1.0	0.39	0.38	0.38	0.39
	1.333	1.42	1.41	1.43	1.43
	1.4	1.65	1.64	1.66	1.66
	2.0	4.05	4.05	4.11	4.08
	2.222	5.18	5.19	5.28	5.22
	2.38	6.09	6.11	6.22	6.12
	2.5	6.84	6.87	6.99	6.87
2.74	0.2	−2.65	−2.67	−2.67	−2.67
	0.4	−1.93	−1.97	−1.97	−1.97
	0.7	−0.98	−1.06	−1.04	−1.03
	0.8	−0.57	−0.65	−0.62	−0.61
	0.9	−0.06	−0.14	−0.08	−0.06
	1.0	0.58	0.52	0.60	0.63
	1.1	1.41	1.35	1.47	1.51

choosing for $\phi(r)$ the Lennard-Jones potential

$$\phi_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{5}$$

where $\sigma = 3.405$ A and $\varepsilon/k_B = 119.8$ K. We have evaluated $\beta\tilde{F}/N$, $\beta P/\rho$ and $\beta U/N$ using for $g_{hs}(r)$ the semiempirical expression proposed by Verlet and Weis ($g_{VW}(r)$) and for S_{hs} the entropy obtained from the Carnaham and Starling equation of state, S_{CS}, corrected by the empirical term proposed by Ross,

$$S_{Soft}/Nk_B = S_{CS}/Nk_B + (\eta/2 + \eta^2 + \eta^4/2) \tag{6}$$

The results are given in Tables 1, 2 and 3 where we also list for comparison the computer simulation results for the equivalent Lennard-Jones fluid (LJ-Sim) as well as those carried out by Ross using for $g_{hs}(r)$ the Percus-Yevick hard-spheres RDF, $g_{PY}(r)$. The comparison shows that both sets of results are very similar and in fair agreement with the LJ-Sim.

Table 2 Pressure PV/Nk_BT as a function of reduced temperature and density. The column headings have the same meaning as those in Table 1.

k_BT/ε	$\rho\sigma^3$	LJ-Sim	Ross	LJ-Ross	DY-Ross
100.00	0.2	1.22	1.22	1.22	1.22
	0.4	1.51	1.50	1.50	1.50
	0.5	1.68	1.67	1.67	1.67
	0.666	2.00	2.01	2.02	2.02
	1.0	2.95	2.96	2.98	2.98
	1.333	4.36	4.40	4.45	4.44
	1.4	4.76	4.76	4.83	4.80
	2.0	9.50	9.56	9.77	9.55
	2.222	12.10	12.26	12.54	12.14
	2.38	14.46	14.56	14.89	14.32
	2.5	16.29	16.54	16.95	16.17
20.00	0.2	1.27	1.26	1.26	1.26
	0.4	1.67	1.65	1.66	1.66
	0.5	1.93	1.92	1.93	1.94
	0.666	2.51	2.51	2.53	2.55
	1.0	4.46	4.49	4.56	4.61
	1.333	8.00	8.09	8.28	8.39
	1.765	16.68	16.75	17.22	17.44
5.00	0.2	1.17	1.15	1.15	1.15
	0.5	1.82	1.82	1.84	1.85
	0.666	2.67	2.67	2.72	2.74
	1.0	6.34	6.49	6.70	6.78
	1.279	13.44	13.46	13.94	14.18
2.74	0.2	0.99	0.96	0.96	0.96
	0.4	1.20	1.14	1.15	1.15
	0.7	2.59	2.57	2.66	2.68
	0.8	3.61	3.65	3.80	3.83
	0.9	5.14	5.21	5.43	5.49
	1.0	7.37	7.37	7.71	7.79
	1.1	10.17	10.30	10.76	10.89

Also, we have carried out one more calculation using for $\phi(r)$ the following DY potential

$$\phi_{\mathrm{DY}}(r) = \left(\frac{E\sigma}{r}\right)\{\exp[-(a/\sigma)(r-\sigma)] - [\exp - (b/\sigma)(r-\sigma)]\} \tag{7}$$

where the various parameters have been chosen to produce close fitting with the Lennard-Jones potential (see Eq. (7)), that is,

$$E = 2.0199\varepsilon,\ a = 14.735,\ b = 2.6793,\ \varepsilon/k_B = 119.8\ \mathrm{K}$$

Table 3 Excess internal energy U/Nk_BT as a function of reduced temperature and density. The column headings have the same meaning as those in Table 1.

k_BT/ε	$\rho\sigma^3$	LJ-Sim	Ross	LJ-Ross	DY-Ross
100.00	0.2	0.036	0.034	0.034	0.035
	0.4	0.085	0.081	0.081	0.084
	0.5	0.115	0.111	0.111	0.116
	0.666	0.175	0.173	0.174	0.181
	1.0	0.361	0.376	0.362	0.377
	1.333	0.648	0.652	0.665	0.692
	1.4	0.734	0.729	0.744	0.773
	2.0	1.767	1.779	1.827	1.890
	2.222	2.346	2.385	2.452	2.526
	2.38	2.887	2.909	2.989	3.071
	2.5	3.304	3.365	3.462	3.541
20.00	0.2	−0.005	−0.010	−0.010	−0.010
	0.4	0.009	0.001	0.012	0.001
	0.5	0.026	0.018	0.019	0.019
	0.666	0.083	0.074	0.077	0.078
	1.0	0.348	0.343	0.357	0.364
	1.333	0.942	0.958	0.999	1.024
	1.765	2.65	2.65	2.762	2.844
5.00	0.2	−0.202	−0.200	−0.201	−0.201
	0.5	−0.474	−0.488	−0.487	−0.489
	0.666	−0.584	−0.592	−0.585	−0.588
	1.0	−0.456	−0.448	−0.409	−0.409
	1.279	0.435	0.413	0.515	0.525
2.74	0.2	−0.440	−0.410	−0.411	−0.412
	0.4	−0.865	−0.855	−0.856	−0.858
	0.7	−1.424	−1.454	−1.444	−1.444
	0.8	−1.562	−1.577	−1.555	−1.554
	0.9	−1.609	−1.622	−1.583	−1.582
	1.00	−1.525	−1.559	−1.498	−1.497
	1.1	−1.351	−1.352	−1.262	−1.261

and

$$\sigma = 3.405\ \text{Å}.$$

The important feature of this pair potential is that it allows all the variational integrals to be determined analytically. The analytical expressions for $\beta\tilde{F}/N$ and $\beta P/\rho$ are given in GS's paper. The results achieved with this pair potential are also given in Tables 1, 2 and 3. As can be seen these new results are very similar to the ones previously obtained with $\phi_{LJ}(r)$ and also are in good accord with the LJ-Sim. This is very important because the amount of computational work involved using $\phi_{DY}(r)$ instead of $\phi_{LJ}(r)$ is considerably reduced. The DY potential then, is specially suitable to study binary liquid mixtures. The preceeding results also show that while $g_{PY}(r)$ is not the best hard-sphere RDF, it is appropriate when used in conjunction with the variational theory in predicting the thermodynamic properties of simple liquids.

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