An extensive study of the Helmholtz free energy of Lennard–Jones fluids using WCA theory

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Abstract

On the basis of results from molecular dynamics and using Weeks–Chandler–Andersen theory, a simple and exact analytical expression for the Helmholtz free energy of a system of particles interacting through the Lennard–Jones potential is obtained for a wide range of densities and temperatures. The values obtained from this expression and its derivative, the potential energy, are compared with existing published values, and are in reasonable agreement. The combination of accuracy with simplicity—only five parameters are used — could be very useful in theoretical and chemical engineering applications, where straightforward mathematical handling of thermodynamic properties is an important requirement.

The high temperature approximation for the radial distribution function and for the Helmholtz free energy are compared with results from exact calculation. The results show this approximation to work well for the radial distribution function at high densities only, but to be good even at low densities for the Helmholtz free energy.

Keywords: Helmholz free energy; High temperature approximation; Lennard–Jones fluids; Molecular dynamics, Radial distribution function; Weeks–Chandler–Andersen theory

1. Introduction

The interpretation of the thermodynamic properties of simple liquids and liquid mixtures has been widely studied by both theoretical and computer-simulation

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methods. The Lennard–Jones (LJ) (12–6) potential is a suitable model for these purposes [1], and it has also been extensively used to model the reference fluid in perturbation treatments of more complex fluids. For chemical engineering applications and for theoretical tests it is very important to have an exact, easy to handle expression for the Helmholtz free energy (HFE) with a wide range of validity, because all other thermodynamic properties — the equation of state (EOS), specific heat, phase equilibrium calculations, etc. — are derived from it by means of standard mathematical relationships.

In the present work we used the Weeks-Chandler-Andersen (WCA) theory [2] of simple fluids to obtain an equation for the HFE as a function of density and temperature by fitting computer simulation results. This involved a great deal of computational effort, since we simulated 269 states for 5000 time steps, corresponding to a LJ system, and for five values of the WCA perturbative parameter λ. We determined the radial distribution function (RDF) data as functions of interparticle distance and λ for each state, and were thus able to determine the HFE using the expressions from WCA theory. We also analysed the high temperature approximation (HTA) for the RDF and HFE.

The remainder of the paper is organized as follows. In the next section, we discuss the more important aspects of WCA theory and the exact expression for the HFE. In the following section, we describe the molecular dynamics (MD) procedure for determination of thermodynamic properties, as well as the analytical expressions for these quantities. The high temperature approximation for RDF and HFE is also analysed. Finally the results are compared with others taken from the literature and the conclusions are summarized. In particular, the analytical expression proposed here for the HFE is the first to be based on a hybrid method — WCA theory and computer simulation results. It thus has a theoretical foundation, and is valid over a wide range of temperatures and densities, as well as having the advantage of mathematical simplicity.

2. WCA theory and the Helmholtz free energy

In WCA perturbation theory, the intermolecular potential, U, which is assumed to be pairwise additive, is separated into a reference part, U_0 and a perturbation part, U_p. While the way in which the two terms are taken account is different for each perturbative theory, all start from the old idea of van der Waals equation, i.e. the separation of the repulsive and attractive interactions, and hence the possibility of studying the properties of a system by taking the effect of the attractive forces, which are small at high densities, to be a perturbation of the repulsive contribution. The usual method is to use a λ or high-temperature expansion [3]. Here the intermolecular potential is written as

$$U(r) = U_0(r) + \lambda U_p(r) \tag{1}$$

where r is the interparticle distance and λ is a perturbative parameter which varies continuously from $\lambda = 0$ (the reference system) to $\lambda = 1$ (the full system).

The WCA theory uses the Lennard–Jones potential given by

$$U_{LJ} = 4[(1/r)^{12} - (1/r)^6] \tag{2}$$

so that the reference potential is

$$U_0(r) = U_{LJ}(r) + 1 \quad \text{if} \quad r \le r_m = 2^{1/6}$$
$$= 0 \quad \text{if} \quad r > r_m \tag{3}$$

and contains all the repulsive interactions, while the perturbation is expressed by

$$U_p(r) = -1 \quad \text{if} \quad r \le r_m$$
$$= U_{LJ}(r) \quad \text{if} \quad r > r_m \tag{4}$$

and contains all the attractive interactions. Here r_m is the distance at which the potential has a minimum, i.e. the distance at which the forces change from repulsive to attractive. In the above and following equations all the properties are expressed in reduced LJ units; for example, energies and distances are in unit of ε (the well depth) and σ (the distance at which the potential is zero), respectively.

To calculate the thermodynamic properties of the system, the WCA perturbation theory gives the following exact expression for the excess (over the ideal gas) of the HFE per particle [4]:

$$A/T = A_0/T - \rho \alpha(T, \rho)/T \tag{5}$$

where A is the HFE per particle of the full LJ system, A_0 that of the reference system, $(\lambda = 0)$, T is temperature, ρ the density and $\alpha(T, \rho)$ is a temperature and density function which includes the perturbative effects of the attractive forces given by

$$\alpha(T, \rho) = -(I_1 + I_2)/\rho \tag{6}$$

I_1 and I_2 being the integrals [5]:

$$I_1 = 2\pi\rho \int r^2 U_p(r) g_0(r)\, dr \tag{7}$$

and

$$I_2 = 2\pi\rho \int_0^1 d\lambda \int r^2 U_p [g_\lambda(r) - g_0(r)]\, dr \tag{8}$$

where $g_\lambda(r)$ and $g_0(r)$ are the RDF of the perturbed $(\lambda \ne 0)$ and reference $(\lambda = 0)$ systems, respectively.

The first problem of all perturbation theories is that the properties of the reference system are unknown. Fortunately in the present case, a connection can be made with the hard sphere (HS) system by means of the Carnahan–Starling (CS) [6] equation of state:

$$Z_0(y) = (1 + y + y^2 - y^3)/(1 - y)^3 \tag{9}$$

where $Z_0 = P_0/\rho T$ is the compressibility factor of the reference system, $y = \pi d^3 \rho/6$ is the packing fraction and d is the HS diameter chosen in an appropriate way. The Verlet–Weis criterion [7]

$$d = (0.3837 + 1.068/T)/(0.4293 + 1/T) \tag{10}$$

that relates the HS diameter with the temperature has been shown to be an excellent procedure for this last choice [8,9].

The HFE per particle of the reference system, A_0, can be obtained from the equation

$$\partial(A_0/T)/\partial\rho = (Z_0 - 1)/\rho \tag{11}$$

that relates the HFE with the compressibility factor Z_0. By integration of Eq. (11) between zero and ρ and making use of Eq. (9) we obtain:

$$\frac{A_0}{T} = -3 + 2(1 - y)^{-1} + (1 - y)^{-2} \tag{12}$$

The second problem is to calculate the effects of the perturbation on the RDF and on the thermodynamic properties. From Eqs. (5) to (8) one can see that to calculate A it is necessary to know the RDFs for each value of density, temperature, interparticle potential and perturbative parameter. Theoretically an approximate method for calculating this function was proposed in WCA theory, the so-called high-temperature approximation (HTA) of RDF [2]. The physical argument of the HTA is that when the temperature and density of a fluid are high, its structure is mainly determined by the strong repulsive forces. Hence the WCA theory proposes that

$$g_\lambda(r) \simeq g_0(r) \tag{13}$$

In an analogous way, the HTA for the HFE is equivalent to assuming that I_2 in Eqs. (5) and (6) is equal to zero.

The validity of both the WCA theory and the HTA for the RDF and the HFE has been analysed in two-dimensional (2D) LJ fluids [8, 10, 11] as well as in some regions — triple point zone — for three-dimensional (3D) LJ fluids [4,5]. In the present work we made an exhaustive analysis of these properties on a very wide region of phase plane for 3D LJ fluids. The results obtained will be dealt with in the next section.

3. Molecular dynamic results, high temperature approximation and analytical expressions

3.1. Molecular dynamics results

Molecular dynamics calculations were performed in order to obtain the RDF of a 3D LJ fluid over a broad range of density and temperature, and for five values of the perturbation parameter ($\lambda = 0, 0.25, 0.5, 0.75$, and 1). The simulation characteristics were similar to those described in Ref. [10]. The number of particles was 504 in all runs, periodic boundary conditions were used and the potential cutoff was $r_c = 2.5$. The total number of time steps was 5000 for each run, with each time step $= 0.005$. To ensure

equilibrium, we followed a temperature scaling procedure [5]. The states simulated are shown in Fig. 1, where some liquid–vapour coexistence points [12] are also plotted.

For each run, $g_\lambda(r)$ and $g_0(r)$ were obtained at intervals of $\Delta r = 0.02$ units of interparticle distance using

$$g_\lambda(r) = n_\lambda(r)/(4\pi r^2 \rho \Delta r) \qquad (14)$$

where $n_\lambda(r)$ is the time-averaged number of particles at distances between r and $r + \Delta r$ from a given particle. The statistical error was estimated to be of the order of 1% [13].

The integrals I_1 and I_2, Eqs. (7) and (8), enable us to calculate the perturbation contribution to A, given by

$$\Delta A = A - A_0 = I_1 + I_2 \qquad (15)$$

The values of these integrals as well as the $\alpha(T,\rho)$ function were calculated from $g_\lambda(r)$ and $g_0(r)$ computer simulation results. Table 1 lists the values of I_1, I_2, $\alpha(T,\rho)$, ΔA and A for the thermodynamic states studied here. The effects of the potential truncation on the HFE were taken into account using the corresponding asymptotic contribution (AC) by assuming that the pair correlation function is unity $(g_\lambda(r) = 1)$ for $r > r_c$:

$$AC = \tfrac{8}{9}\pi\rho[(1/r_c)^9 - 3(1/r_c)^3] \qquad (16)$$

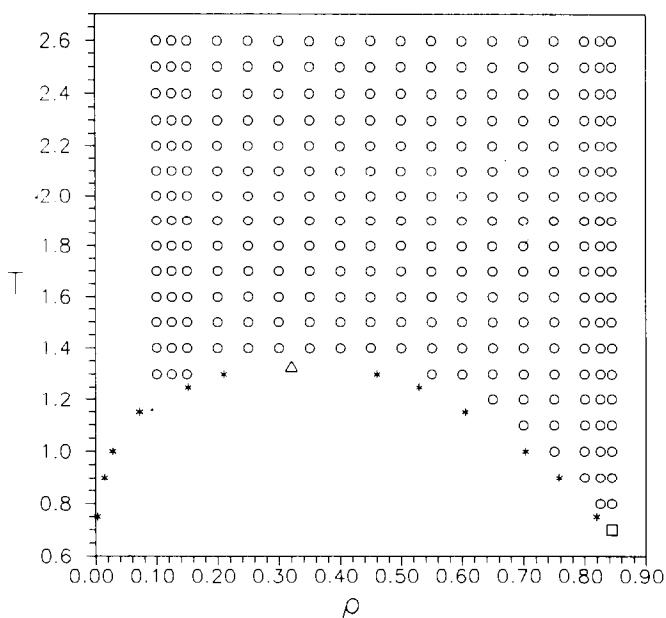where r_c is the cutoff distance.

Fig. 1. Simulated states in this work (○), coexistence line (∗) from Ref. [12] critical point (△) from Ref. [17] and triple point (□) from Ref. [13].

Table 1
Simulated results. Integrals I_1 and I_2 given by Eqs. (7) and (8), respectively; function $\alpha(T,\rho)$ obtained from Eq. (6); the contribution, ΔA, of the perturbation of the HFE Eq. (15); the total HFE, A, from Eqs. (12), (15) and (16).

T	ρ	$-I_1$	$-I_2$	α	ΔA	A
0.7	0.800	5.731	0.011	7.178	− 5.473	− 3.349
	0.825	5.933	0.012	7.206	− 5.945	− 3.369
	0.844	6.095	0.011	7.235	− 6.106	− 3.381
0.8	0.800	5.711	0.011	7.153	− 5.723	− 3.011
	0.825	5.921	0.010	7.189	− 5.931	− 3.018
	0.844	6.080	0.010	7.216	− 6.090	− 3.013
0.9	0.800	5.704	0.010	7.142	− 5.714	− 2.697
	0.825	5.910	0.009	7.174	− 5.919	− 2.682
	0.844	6.066	0.009	7.197	− 6.047	− 2.659
1.0	0.750	5.281	0.010	7.054	− 5.291	− 2.407
	0.800	5.689	0.010	7.124	− 5.699	− 2.387
	0.825	5.897	0.009	7.158	− 5.905	− 2.356
	0.844	6.045	0.010	7.174	− 6.055	− 2.314
1.1	0.700	4.943	0.013	7.081	− 4.957	− 2.222
	0.750	5.273	0.009	7.042	− 5.282	− 2.143
	0.800	5.680	0.009	7.111	− 5.689	− 2.091
	0.825	5.885	0.008	7.143	− 5.893	− 2.042
	0.844	6.036	0.008	7.162	− 6.044	− 1.989
1.2	0.650	4.449	0.014	6.867	− 4.464	− 1.889
	0.700	4.857	0.011	6.954	− 4.867	− 1.910
	0.750	5.265	0.010	7.033	− 5.275	− 1.887
	0.800	5.673	0.007	7.100	− 5.680	− 1.805
	0.825	5.874	0.007	7.129	− 5.882	− 1.738
	0.844	6.031	0.006	7.154	− 6.038	− 1.677
1.3	0.100	0.530	0.032	5.619	− 0.562	− 0.319
	0.125	0.671	0.036	5.659	− 0.707	− 0.397
	0.150	0.822	0.044	5.770	− 0.866	− 0.485
	0.550	3.641	0.023	6.661	− 3.664	− 1.582
	0.600	4.042	0.017	6.765	− 4.059	− 1.653
	0.650	4.443	0.013	6.856	− 4.456	− 1.688
	0.700	4.852	0.009	6.945	− 4.861	− 1.687
	0.750	5.260	0.008	7.024	− 5.268	− 1.638
	0.800	5.662	0.008	7.088	− 5.670	− 1.524
	0.825	5.868	0.007	7.121	− 5.875	− 1.445
	0.844	6.015	0.008	7.136	− 6.023	− 1.365
1.4	0.100	0.520	0.031	5.519	− 0.552	− 0.289
	0.125	0.673	0.033	5.644	− 0.706	− 0.370
	0.150	0.819	0.039	5.724	− 0.857	− 0.285
	0.200	1.125	0.048	5.865	− 1.173	− 0.600
	0.250	1.442	0.051	5.973	− 1.493	− 0.744
	0.300	1.782	0.046	6.092	− 1.828	− 0.886
	0.350	2.136	0.044	6.228	− 2.180	− 1.027
	0.400	2.498	0.036	6.335	− 2.534	− 1.150
	0.450	2.868	0.031	6.443	− 2.899	− 1.260
	0.500	3.253	0.024	6.555	− 3.277	− 1.358
	0.550	3.639	0.020	6.654	− 3.660	− 1.431
	0.600	4.036	0.017	6.755	− 4.053	− 1.479

Table 1 (*Continued*)

T	ρ	$-I_1$	$-I_2$	α	ΔA	A
	0.650	4.442	0.013	6.853	− 4.455	− 1.498
	0.700	4.846	0.009	6.837	− 4.856	− 1.470
	0.750	5.253	0.008	7.014	− 5.261	− 1.394
	0.800	5.653	0.008	7.076	− 5.661	− 1.251
	0.825	5.856	0.007	7.107	− 5.863	− 1.155
	0.844	6.009	0.006	7.127	− 6.015	− 1.076
1.5	0.100	0.528	0.027	5.549	− 0.555	− 0.273
	0.125	0.670	0.030	5.603	− 0.700	− 0.340
	0.150	0.818	0.038	5.705	− 0.856	− 0.414
	0.200	1.128	0.041	5.846	− 1.169	− 0.554
	0.250	1.452	0.043	5.980	− 1.495	− 0.692
	0.300	1.795	0.044	6.128	− 1.838	− 0.829
	0.350	2.138	0.036	6.211	− 2.174	− 0.941
	0.400	2.493	0.033	6.317	− 2.527	− 1.048
	0.450	2.870	0.029	6.444	− 2.900	− 1.151
	0.500	3.251	0.023	6.548	− 3.274	− 1.228
	0.550	3.640	0.019	6.652	− 3.658	− 1.283
	0.600	4.037	0.014	6.752	− 4.051	− 1.312
	0.650	4.435	0.012	6.841	− 4.447	− 1.304
	0.700	4.839	0.010	6.927	− 4.849	− 1.255
	0.750	5.240	0.009	6.998	− 5.249	− 1.150
	0.800	5.646	0.007	7.067	− 5.653	− 0.984
	0.825	5.846	0.007	7.094	− 5.853	− 0.872
	0.844	6.000	0.006	7.117	− 6.006	− 0.775
1.6	0.100	0.527	0.027	5.537	− 0.554	− 0.252
	0.125	0.671	0.029	5.607	− 0.701	− 0.316
	0.150	0.832	0.032	5.760	− 0.864	− 0.393
	0.200	1.135	0.037	5.856	− 1.171	− 0.515
	0.250	1.447	0.041	5.950	− 1.487	− 0.631
	0.300	1.787	0.040	6.093	− 1.828	− 0.754
	0.350	2.145	0.035	6.227	− 2.180	− 0.868
	0.400	2.498	0.033	6.327	− 2.531	− 0.959
	0.450	2.867	0.028	6.433	− 2.895	− 1.037
	0.500	3.245	0.024	6.538	− 3.269	− 1.071
	0.550	3.635	0.018	6.641	− 3.652	− 1.108
	0.600	4.034	0.013	6.745	− 4.047	− 1.147
	0.650	4.434	0.010	6.837	− 4.444	− 1.119
	0.700	4.837	0.009	6.922	− 4.845	− 1.047
	0.750	5.241	0.007	6.998	− 5.249	− 0.922
	0.800	5.639	0.007	7.058	− 5.646	− 0.724
	0.825	5.838	0.006	7.084	− 5.844	− 0.596
	0.844	5.986	0.007	7.101	− 5.993	− 0.484
1.7	0.100	0.537	0.021	5.586	− 0.559	− 0.238
	0.125	0.678	0.029	5.657	− 0.707	− 0.298
	0.150	0.824	0.034	5.719	− 0.858	− 0.357
	0.200	1.135	0.035	5.851	− 1.170	− 0.474
	0.250	1.424	0.036	6.000	− 1.500	− 0.592
	0.300	1.796	0.034	6.100	− 1.830	− 0.691
	0.350	2.141	0.033	6.210	− 2.173	− 0.783
	0.400	2.498	0.030	6.318	− 2.527	− 0.863

Table 1 (*Continued*)

T	ρ	$-I_1$	$-I_2$	α	ΔA	A
	0.450	2.866	0.026	6.427	− 2.892	− 0.927
	0.500	3.246	0.021	6.535	− 3.268	− 0.973
	0.550	3.638	0.016	6.643	− 3.654	− 0.996
	0.600	4.034	0.013	6.745	− 4.047	− 0.988
	0.650	4.430	0.010	6.832	− 4.441	− 0.937
	0.700	4.830	0.009	6.912	− 4.838	− 0.839
	0.750	5.231	0.008	6.985	− 5.239	− 0.688
	0.800	5.630	0.008	7.047	− 5.637	− 0.466
	0.825	5.827	0.008	7.072	− 5.835	− 0.325
	0.844	5.979	0.007	7.093	− 5.986	− 0.205
1.8	0.100	0.540	0.020	5.598	− 0.560	− 0.220
	0.125	0.676	0.028	5.637	− 0.705	− 0.272
	0.150	0.830	0.029	5.727	− 0.859	− 0.329
	0.200	1.140	0.031	5.854	− 1.171	− 0.435
	0.250	1.460	0.032	5.971	− 1.493	− 0.533
	0.300	1.796	0.032	6.095	− 1.828	− 0.625
	0.350	2.140	0.032	6.206	− 2.172	− 0.705
	0.400	2.502	0.027	6.325	− 2.530	− 0.774
	0.450	2.870	0.023	6.431	− 2.894	− 0.823
	0.500	3.249	0.019	6.535	− 3.268	− 0.851
	0.550	3.638	0.015	6.643	− 3.654	− 0.857
	0.600	4.029	0.013	6.736	− 4.042	− 0.825
	0.650	4.427	0.010	6.826	− 4.437	− 0.756
	0.700	4.829	0.007	6.909	− 4.836	− 0.639
	0.750	5.229	0.006	6.980	− 5.235	− 0.463
	0.800	5.628	0.006	7.042	− 5.634	− 0.218
	0.825	5.822	0.006	7.064	− 5.828	− 0.061
	0.844	5.971	0.006	7.082	− 5.977	− 0.072
1.9	0.100	0.542	0.019	5.616	− 0.562	− 0.202
	0.125	0.682	0.022	5.637	− 0.705	− 0.248
	0.150	0.825	0.029	5.698	− 0.855	− 0.296
	0.200	1.141	0.031	5.861	− 1.172	− 0.396
	0.250	1.470	0.030	6.000	− 1.500	− 0.489
	0.300	1.795	0.031	6.086	− 1.826	− 0.560
	0.350	2.149	0.026	6.214	− 2.175	− 0.632
	0.400	2.508	0.025	·6.333	− 2.533	− 0.687
	0.450	2.868	0.023	6.425	− 2.891	− 0.715
	0.500	3.251	0.017	6.537	− 3.296	− 0.732
	0.550	3.637	0.014	6.638	− 3.651	− 0.717
	0.600	4.024	0.013	6.727	− 4.036	− 0.664
	0.650	4.422	0.009	6.817	− 4.431	− 0.576
	0.700	4.823	0.007	6.901	− 4.830	− 0.438
	0.750	5.219	0.007	6.969	− 5.226	− 0.237
	0.800	5.617	0.006	7.029	− 5.623	0.034
	0.825	5.815	0.007	7.057	− 5.822	0.199
	0.844	5.966	0.006	7.076	− 5.972	0.341
2.0	0.100	0.542	0.017	5.589	− 0.559	− 0.182
	0.125	0.685	0.024	5.672	− 0.709	− 0.229
	0.150	0.832	0.027	5.722	− 0.858	− 0.270
	0.200	1.140	0.029	5.845	− 1.169	− 0.354

Table 1 (Continued)

T	ρ	$-I_1$	$-I_2$	α	ΔA	A
	0.250	1.467	0.030	5.989	− 1.497	− 0.435
	0.300	1.796	0.030	6.086	− 1.826	− 0.497
	0.350	2.142	0.027	6.179	− 2.169	− 0.550
	0.400	2.499	0.026	6.311	− 2.525	− 0.590
	0.450	2.869	0.021	6.421	− 2.980	− 0.611
	0.500	3.248	0.017	6.531	− 3.265	− 0.609
	0.550	3.634	0.015	6.634	− 3.649	− 0.579
	0.600	4.025	0.011	6.728	− 4.037	− 0.512
	0.650	4.422	0.009	6.817	− 4.431	− 0.403
	0.700	4.814	0.009	6.891	− 4.824	− 0.240
	0.750	5.215	0.006	6.962	− 5.221	− 0.017
	0.800	5.612	0.006	7.022	− 5.618	0.277
	0.825	5.805	0.007	7.045	− 5.812	0.460
	0.844	5.956	0.005	7.064	− 5.962	0.611
2.1	0.100	0.542	0.017	5.596	− 0.560	− 0.165
	0.125	0.691	0.021	5.697	− 0.712	− 0.208
	0.150	0.831	0.025	5.706	− 0.856	− 0.240
	0.200	1.147	0.025	5.861	− 1.172	− 0.318
	0.250	1.464	0.030	5.974	− 1.493	− 0.381
	0.300	1.790	0.031	6.070	− 1.821	− 0.430
	0.350	2.145	0.024	6.198	− 2.169	− 0.475
	0.400	2.502	0.024	6.314	− 2.526	− 0.503
	0.450	2.871	0.019	6.424	− 2.891	− 0.509
	0.500	3.248	0.017	6.530	− 3.265	− 0.491
	0.550	3.636	0.012	6.633	− 3.648	− 0.444
	0.600	4.023	0.014	6.728	− 4.037	− 0.360
	0.650	4.420	0.008	6.812	− 4.428	− 0.230
	0.700	4.814	0.008	6.888	− 4.822	− 0.047
	0.750	5.210	0.007	6.955	− 5.217	0.198
	0.800	5.607	0.006	7.015	− 5.612	0.518
	0.825	5.800	0.006	7.038	− 5.806	0.713
	0.844	5.953	0.005	7.059	− 5.958	0.871
2.2	0.100	0.541	0.016	5.574	− 0.557	− 0.143
	0.125	0.679	0.021	5.603	− 0.700	− 0.173
	0.150	0.836	0.025	5.737	− 0.861	− 0.217
	0.200	1.141	0.028	5.842	− 1.168	− 0.275
	0.250	1.461	0.027	5.953	− 1.488	− 0.326
	0.300	1.795	0.026	6.073	− 1.822	− 0.369
	0.350	2.143	0.020	6.197	− 2.169	− 0.401
	0.400	2.498	0.023	6.304	− 2.521	− 0.411
	0.450	2.868	0.020	6.417	− 2.888	− 0.404
	0.500	3.245	0.016	6.522	− 3.261	− 0.370
	0.550	3.628	0.015	6.624	− 3.643	− 0.306
	0.600	4.021	0.010	6.719	− 4.031	− 0.204
	0.650	4.315	0.009	6.805	− 4.423	− 0.056
	0.700	4.813	0.006	6.885	− 4.820	0.143
	0.750	5.206	0.006	6.950	− 5.213	0.412
	0.800	5.600	0.005	7.007	− 5.605	0.757
	0.825	5.789	0.007	7.025	− 5.796	0.967
	0.844	5.943	0.005	7.048	− 5.649	1.134

Table 1 (*Continued*)

T	ρ	$-I_1$	$-I_2$	α	ΔA	A
2.3	0.100	0.540	0.016	5.572	-0.557	-0.125
	0.125	0.691	0.018	5.668	-0.708	-0.158
	0.150	0.834	0.023	5.717	-0.858	-0.186
	0.200	1.150	0.023	5.863	-1.173	-0.241
	0.250	1.470	0.025	5.981	-1.495	-0.284
	0.300	1.806	0.023	6.098	-1.829	-0.315
	0.350	2.143	0.024	6.190	-2.167	-0.326
	0.400	2.505	0.019	6.310	-2.524	-0.327
	0.450	2.872	0.018	6.421	-2.889	-0.304
	0.500	3.245	0.015	6.521	-3.260	-0.253
	0.550	3.634	0.012	6.629	-3.646	-0.177
	0.600	4.019	0.011	6.715	-4.029	-0.053
	0.650	4.413	0.008	6.801	-4.421	0.113
	0.700	4.808	0.006	6.877	-4.814	0.336
	0.750	5.202	0.006	6.944	-5.208	0.624
	0.800	5.595	0.004	7.000	-5.600	0.992
	0.825	5.784	0.006	7.018	-5.790	1.214
	0.844	5.937	0.005	7.040	-5.941	1.393
2.4	0.100	0.539	0.018	5.572	-0.557	-0.107
	0.125	0.685	0.018	5.626	-0.703	-0.130
	0.150	0.689	0.017	5.733	-0.860	-0.160
	0.200	1.142	0.025	5.835	-1.167	-0.197
	0.250	1.465	0.027	5.966	-1.492	-0.232
	0.300	1.801	0.025	6.087	-1.826	-0.252
	0.350	2.146	0.024	6.200	-2.170	-0.256
	0.400	2.508	0.019	6.316	-2.526	-0.243
	0.450	2.874	0.018	6.426	-2.892	-0.207
	0.500	3.249	0.013	6.524	-3.262	-0.140
	0.550	3.629	0.012	6.620	-3.641	-0.041
	0.600	4.015	0.009	6.708	-4.025	0.098
	0.650	4.410	0.007	6.797	-4.418	0.281
	0.700	4.803	0.007	6.872	-4.810	0.524
	0.750	5.195	0.006	6.935	-5.201	0.836
	0.800	5.587	0.005	6.990	-5.592	1.227
	0.825	5.779	0.005	7.011	-5.784	1.459
	0.844	5.930	0.005	7.031	-5.934	1.648
2.5	0.100	0.545	0.014	5.595	-0.560	-0.092
	0.125	0.690	0.017	5.660	-0.708	-0.113
	0.150	0.840	0.019	5.727	-0.859	-0.131
	0.200	1.142	0.026	5.841	-1.168	-0.160
	0.250	1.468	0.023	5.966	-1.492	-0.183
	0.300	1.806	0.023	6.097	-1.829	-0.194
	0.350	2.148	0.022	6.199	-2.170	-0.183
	0.400	2.511	0.019	6.231	-2.529	-0.160
	0.450	2.870	0.016	6.414	-2.886	-0.102
	0.500	3.246	0.014	6.519	-3.259	-0.023
	0.550	3.630	0.012	6.621	-3.641	-0.088
	0.600	4.015	0.010	6.707	-4.024	0.335
	0.650	4.404	0.008	6.788	-4.412	0.451
	0.700	4.796	0.007	6.862	-4.803	0.714

Table 1 (Continued)

T	ρ	$-I_1$	$-I_2$	α	ΔA	A
	0.750	5.190	0.006	6.928	− 5.196	1.045
	0.800	5.582	0.004	6.983	− 5.586	1.458
	0.825	5.775	0.004	7.005	− 5.779	1.701
	0.844	5.922	0.004	7.021	− 5.926	1.901
2.6	0.100	0.544	0.015	5.583	− 0.558	− 0.072
	0.125	0.693	0.016	5.668	− 0.708	− 0.090
	0.150	0.842	0.019	5.735	− 0.860	− 0.105
	0.200	1.146	0.022	5.841	− 1.168	− 0.123
	0.250	1.470	0.021	5.967	− 1.492	− 0.134
	0.300	1.805	0.022	6.092	− 1.827	− 0.132
	0.350	2.153	0.019	6.207	− 2.183	− 0.114
	0.400	2.509	0.020	6.319	− 2.528	− 0.074
	0.450	2.869	0.017	6.412	− 2.885	− 0.003
	0.500	3.247	0.014	6.521	− 3.261	0.088
	0.550	3.630	0.010	6.618	− 3.640	0.128
	0.600	4.016	0.008	6.707	− 4.024	0.391
	0.650	4.403	0.007	6.785	− 4.410	0.616
	0.700	4.791	0.007	6.855	− 4.798	0.901
	0.750	5.185	0.006	6.921	− 5.191	1.252
	0.800	5.574	0.005	6.974	− 5.597	1.689
	0.825	5.768	0.005	6.997	− 5.773	1.942
	0.844	5.907	0.006	7.006	− 5.913	2.158

3.2. Validity of the HTA

In order to analyse the HTA for the RDF, we calculated the difference

$$\Delta g_\lambda(r_1) = g_\lambda(r_1) - g_0(r_1) \tag{17}$$

between the maximum values of the RDFs of the system (r_1 is the first maximum position) with $\lambda \neq 0$ and with $\lambda = 0$. Fig. 2 shows the relative deviation

$$100[g(r_1) - g_0(r_1)]/g_0(r_1) \tag{18}$$

for all the simulated states. One can see that the approximation works best in the higher density region. This result is similar to that obtained for a two-dimensional LJ system [8].

As noted above, the HTA for the HFE is equivalent to making I_2 equal to zero in Eq. (15). The two possibilities are either that I_2 is zero because $\Delta g_\lambda(r) = 0$, or that, even with $\Delta g_\lambda(r) \neq 0$, the integral I_2 vanishes. From Table 1 we are able to quantify the deviation caused by using the HTA, i.e., the percentage represented by I_2 relative to A. The discrepancies are shown in Fig. 3. One sees that the HTA is a better approximation for the HFE than for the RDF, since the differences are less than 5% over a wider density range, even reaching densities as low as $\rho = 0.35$.
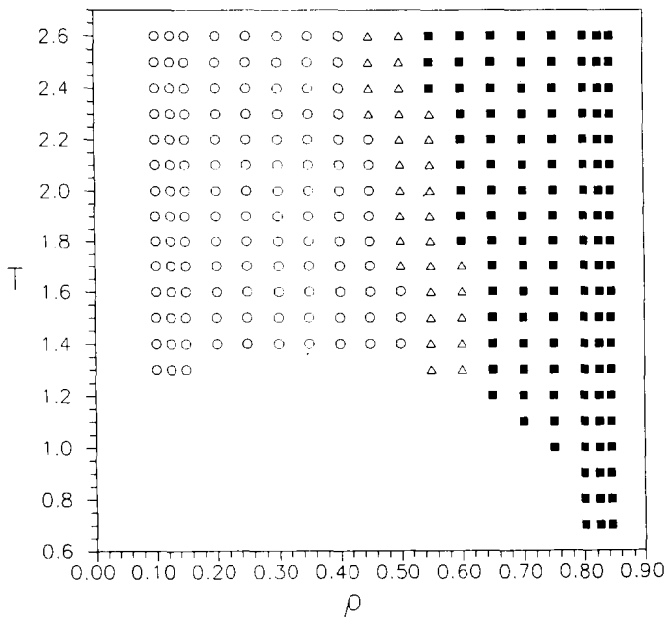
Fig. 2. The HTA deviation applied to the RDF: deviations greater than 10% (○), between 10% and 5% (△), and less than 5% (■).

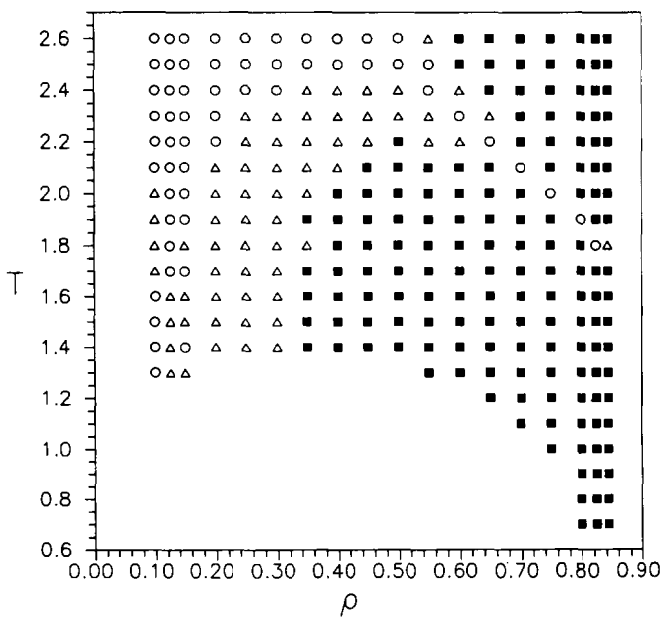Fig. 3. The HTA deviation applied to the HFE: deviations greater than 10% (○), between 10% and 5% (△), and less than 5%(■).

3.3. Analytical expression for the HFE

We shall here propose an analytical expression for the HFE of an LJ system using the WCA separation of the potential. As was mentioned above, the WCA expression for the HFE is given by Eq. (5), A_0 being given by Eq. (12). To test the validitity of Eq. (12), we obtained the values of the internal energy, E_0, of the reference system by differentiating A_0 with respect to T. The resulting expression for E_0 is

$$(E_0)_{cal} = \left[\frac{4 - 2y}{(1-y)^2}\right]\left[\frac{3y}{d}\right]\left[\frac{0.07479}{(0.4293 + 1/T)^2}\right] \tag{19}$$

Values of E_0 from this equation were compared with the MD data for the potential energy per particle of the reference system, $\lambda = 0$ (Table 2). The greatest discrepancies are found for low densities and low temperatures, the relative mean deviation between $(E_0)_{cal}$ and $(E_0)_{MD}$ being around 4%. We can therefore conclude that the Carnahan–

Table 2

Potential energy per particle for the reference system obtained from MD simulation $(E_0)_{MD}$ and from Eq. (18), $(E_0)_{cal}$, for high temperatures.

T	ρ	$(E_0)_{MD}$	$(E_0)_{cal}$
2.0	0.100	0.056	0.060
	0.125	0.072	0.078
	0.150	0.095	0.097
	0.200	0.131	0.139
	0.250	0.177	0.186
	0.300	0.232	0.240
	0.350	0.291	0.303
	0.400	0.357	0.375
	0.450	0.441	0.458
	0.500	0.532	0.554
	0.550	0.635	0.666
	0.600	0.762	0.796
	0.650	0.907	0.949
	0.700	1.089	1.129
	0.750	1.278	1.342
	0.800	1.523	1.596
	0.825	1.650	1.740
	0.844	1.762	1.860
2.1	0.100	0.061	0.063
	0.125	0.082	0.082
	0.150	0.096	0.101
	0.200	0.138	0.145
	0.250	0.186	0.195
	0.300	0.241	0.251
	0.350	0.310	0.317
	0.400	0.377	0.392
	0.450	0.463	0.478
	0.500	0.560	0.578

Table 2 (Continued)

T	ρ	$(E_0)_{MD}$	$(E_0)_{cal}$
	0.550	0.667	0.694
	0.600	0.801	0.829
	0.650	0.950	0.987
	0.700	1.125	1.173
	0.750	1.339	1.393
	0.800	1.573	1.655
	0.825	1.726	1.804
	0.844	1.835	1.926
2.2	0.100	0.062	0.066
	0.125	0.082	0.085
	0.150	0.103	0.106
	0.200	0.147	0.151
	0.250	0.197	0.203
	0.300	0.254	0.262
	0.350	0.317	0.330
	0.400	0.391	0.408
	0.450	0.486	0.497
	0.500	0.589	0.601
	0.550	0.702	0.721
	0.600	0.828	0.861
	0.650	0.988	1.024
	0.700	1.166	1.216
	0.750	1.375	1.442
	0.800	1.656	1.711
	0.825	1.797	1.864
	0.844	1.901	1.990
2.3	0.100	0.067	0.069
	0.125	0.085	0.089
	0.150	0.105	0.110
	0.200	0.153	0.157
	0.250	0.208	0.211
	0.300	0.268	0.273
	0.350	0.333	0.343
	0.400	0.410	0.423
	0.450	0.510	0.516
	0.500	0.615	0.623
	0.550	0.732	0.747
	0.600	0.864	0.891
	0.650	1.036	1.059
	0.700	1.214	1.257
	0.750	1.437	1.489
	0.800	1.701	1.765
	0.825	1.861	1.921
	0.844	1.976	2.051
2.4	0.100	0.069	0.071
	0.125	0.091	0.092
	0.150	0.113	0.114
	0.200	0.161	0.163
	0.250	0.214	0.219
	0.300	0.282	0.283

Table 2 (*Continued*)

T	ρ	$(E_0)_{MD}$	$(E_0)_{cal}$
	0.350	0.350	0.355
	0.400	0.431	0.438
	0.450	0.522	0.534
	0.500	0.639	0.645
	0.550	0.758	0.772
	0.600	0.904	0.921
	0.650	1.075	1.093
	0.700	1.269	1.296
	0.750	1.504	1.535
	0.800	1.783	1.817
	0.825	1.924	1.977
	0.844	2.052	2.109
2.5	0.100	0.072	0.074
	0.125	0.094	0.096
	0.150	0.116	0.118
	0.200	0.168	0.169
	0.250	0.225	0.226
	0.300	0.290	0.292
	0.350	0.363	0.367
	0.400	0.449	0.453
	0.450	0.549	0.552
	0.500	0.653	0.665
	0.550	0.789	0.797
	0.600	0.938	0.949
	0.650	1.112	1.126
	0.700	1.315	1.334
	0.750	1.558	1.578
	0.800	1.836	1.866
	0.825	1.981	2.030
	0.844	2.118	2.164
2.6	0.100	0.075	0.076
	0.125	0.097	0.099
	0.150	0.121	0.123
	0.200	0.172	0.174
	0.250	0.232	0.234
	0.300	0.305	0.302
	0.350	0.377	0.379
	0.400	0.466	0.467
	0.450	0.562	0.568
	0.500	0.682	0.685
	0.550	0.818	0.820
	0.600	0.975	0.976
	0.650	1.156	1.158
	0.700	1.367	1.370
	0.750	1.602	1.620
	0.800	1.887	1.914
	0.825	2.053	2.081
	0.844	2.188	2.218

Starling equation for the HFE, Eq. (12), represents the reference system well, because the results obtained for the potential energy per particle from Eq. (18) are in good agreement with the MD results for this property.

The second step in obtaining the HFE is to find an analytical expression for the function $\alpha(T,\rho)$. This was done by fitting the MD results for $\alpha(T,\rho)$ given by Eq. (6). The corresponding MD values of $\alpha(T,\rho)$ as well as their terms I_1 and I_2, given by Eqs. (7) and (8), are listed in Table 1. For all the thermodynamic states studied here, the result of this fit is:

$$\alpha_{cal}(T,\rho) = C_1(T) + C_2(T)\rho \tag{20}$$

where $C_1(T)$ and $C_2(T)$ are the linear temperature functions

$$C_1(T) = 5.417805 + 0.022211\,T \tag{21a}$$

$$C_2(T) = 2.761161 - 0.106594\,T \tag{21b}$$

The relative mean error of the fit is less than 1%. Fig. 4 and 5 show the values of $\alpha(T,\rho)$ calculated using Eq. (6) and the values obtained from the analytical expression proposed here, Eq. (20).

Finally, from Eq. (5), and taking into account the expressions for A_0, Eq. (12), for $\alpha_{cal}(T,\rho)$ given by eq. (19), and the asymptotic contribution, AC, Eq. (16), we were able to obtain an analytical expression for A as a function of the thermodynamic state
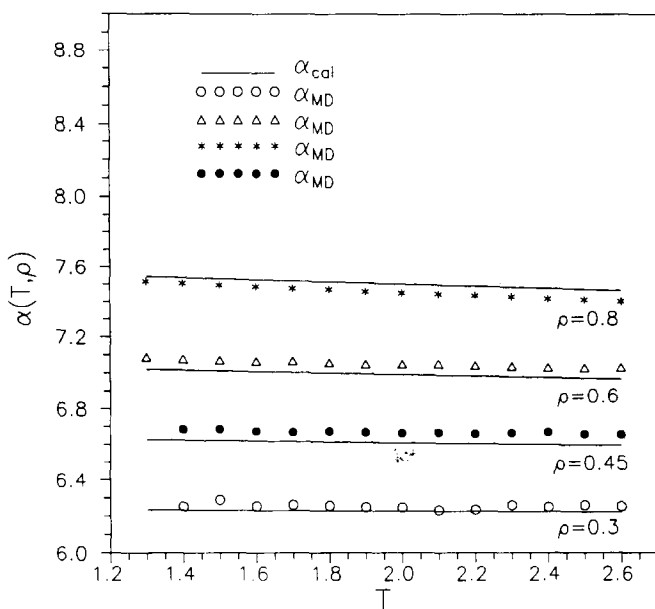
Fig. 4. Function $\alpha(T,\rho)$ versus temperature for densities $\rho = 0.3$, 0.45, 0.60 and 0.80. Symbols represent the MD results, α_{MD}, and lines represent the fitted function α_{cal}.
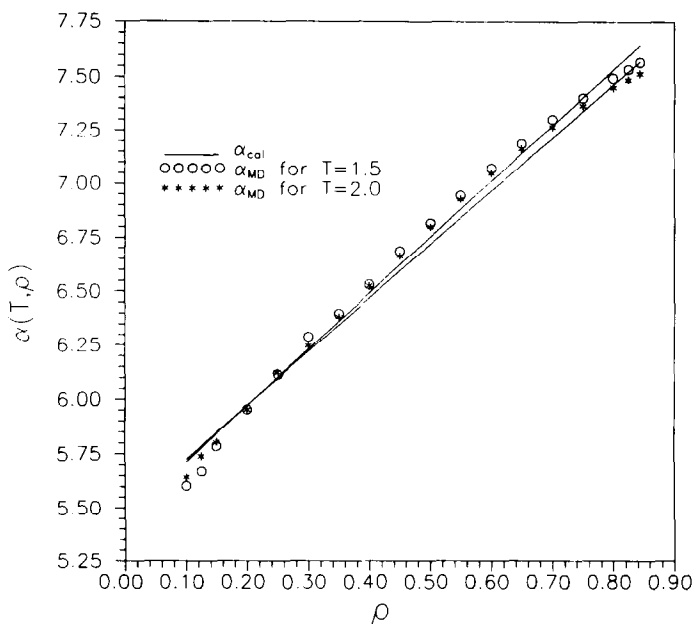
Fig. 5. Function $\alpha(T,\rho)$ versus density for temperatures $T=1.5$ and $T=2.0$. Symbols represent the MD results, α_{MD}, and lines represent the fitted function α_{cal}.

variables:

$$A = A_0 - \rho \alpha_{cal}(T,\rho) + AC \tag{22}$$

or more explicitly,

$$A = T\frac{4y - 3y^2}{(1-y)^2} - [C_1(T) + C_2(T)_p(\text{RHD})]\rho + C_3\rho \tag{23}$$

where $C_1(T)$ and $C_2(T)$ are given by Eqs. (21a) and (21b), respectively, and C_3 is a constant obtained from Eq. (16), related to the asymptotic contribution to the HFE. Taking $r_c = 2.5$, its value is -0.535432.

We followed two procedures in order to check the validity of Eq. (23). the first was to compare the computer MD results for the potential energy per particle for the LJ system with those obtained by differentiating Eq. (23) with respect to T, i.e.,

$$E_{cal} = E_0 - \rho\alpha(T,\rho) + \rho T \frac{\partial}{\partial T}\alpha(T,\rho) \tag{24}$$

As one can see in Figs, 6 and 7, the two values in excellent agreement. The second procedure was to compare our HFE expression, Eq. (23), with other published results: with the Monte Carlo (MC) computer simulations by Levesque and Verlet (LV) [14]
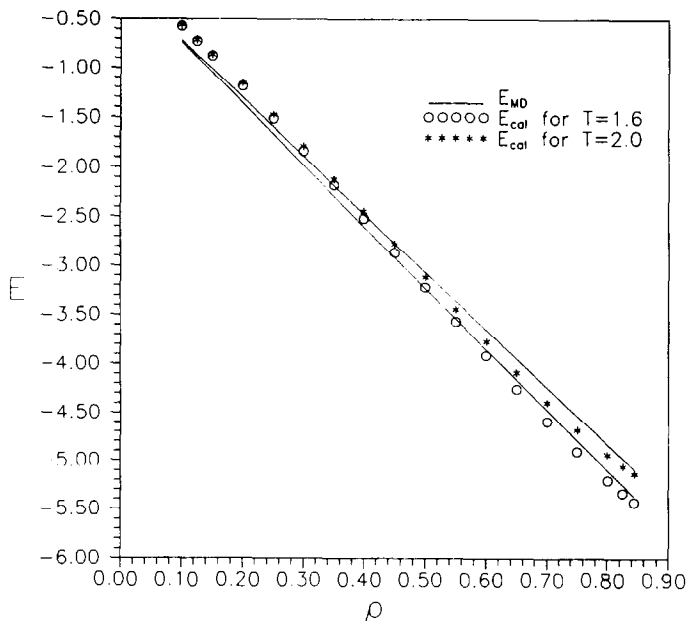
Fig. 6. Potential energy per particle for the full system obtained from the MD simulation (E_{MD}) and form Eq. (24) (E_{cal}) versus density, for temperatures $T = 1.6$ and $T = 2.0$.

and by Adachi and Lu (AL) [15], and with values from the EOS proposed by Johnson et al. (JZG) [16]. Figs. 8a, 8b and 8c show the results of these comparisons. One can see that generally good agreement exists, with the advantage that our HFE equation is easier to handle mathematically.

4. Conclusions

Using WCA theory, we have obtained MD results over a wide range of temperatures and densities which enabled us to analyse separately the effect of the repulsive and attractive forces in the calculation of the HFE. The results confirmed the following. Firstly, the HFE of the reference system — repulsive intermolecular forces only — can be described through a Carnahan–Starling-type equation with the HS diameter given by the Verlet–Weis criterion Eq. (10), over the complete range of temperatures and densities studied. Secondly, the best of the HTA showed that although it is a good approximation for the RDF for high density only, it is a better approximation for the HFE since the differences are less than 5% over a wider density range. Thirdly, the van der Waals model of a fluid, i.e., the approximation $\alpha(T, \rho) = $ constant, is only valid at high densities, as had been noted by Rull *et al.* [5]. Fourthly the analytical expression presented here, Eq. (23) is, at present, the easiest to handle (it has only five constants), is exact, and has a theoretical foundation (WCA theory).
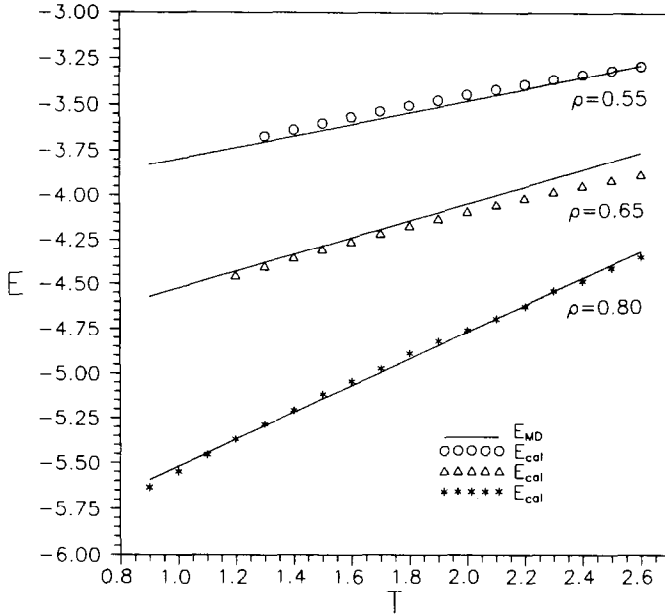
Fig. 7. Potential energy per particle for the full system versus temperature from the MD simulation (E_{MD}) and from Eq. (24) (E_{cal}), for densities $\rho = 0.35, 0.65$ and 0.80.
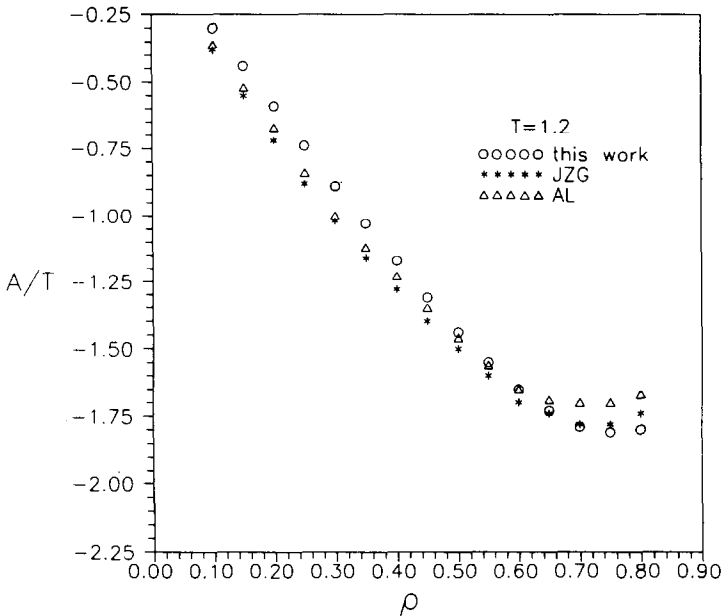

Fig. 8. Helmholtz free energy (A/T) obtained from Johnson et al. (JZG) [16]; Levesque and Verlet, (LV) [14]; Adachi and Lu, (AL) [15] together with the values given by the analytical expression proposed in this work, Eq. (23): (a) for $T = 1.2$, (b) for $T = 1.35$, and (c) for $T = 1.5$.
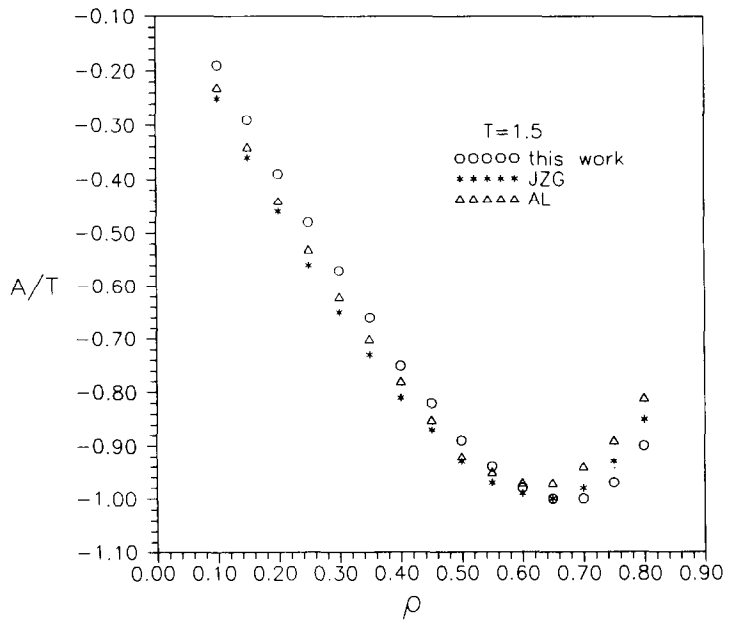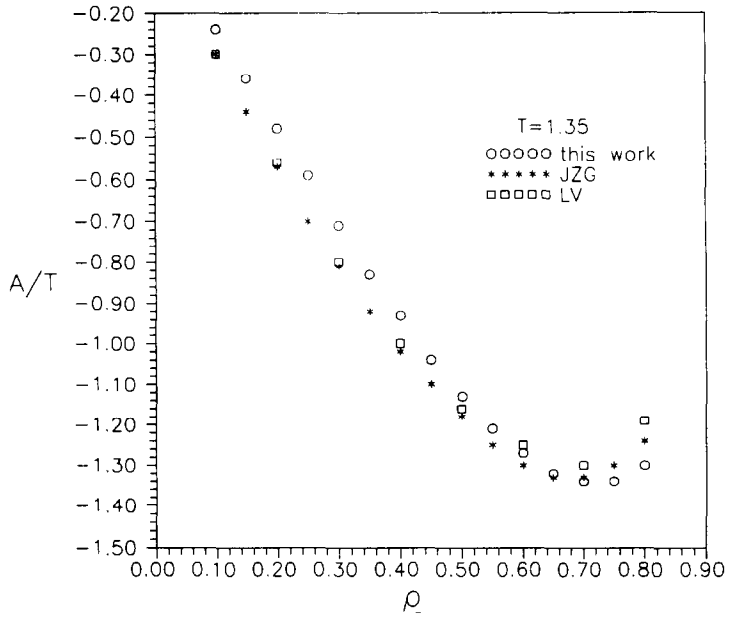
Fig. 8. (*Continued*)

A complete test of other thermodynamic quantities derived from Eq. (23), the EOS, specific heat, liquid–vapour equilibrium, etc., will be made in the near future.

Acknowledgements

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