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Accurate analytical expressions of thermodynamic properties of supercritical Lennard–Jones fluids

F. Cuadros[a,*], W. Ahumada[b]

[a] *Departamento de Física, Universidad de Extremadura, 06071 Badajoz, Spain*
[b] *Departamento de Física, Universidad Católica del Norte, Antofagasta, Chile*

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Abstract

Extensive computer simulations have been carried out in order to obtain analytical expressions for such thermodynamic properties as the Helmholtz free energy, internal energy, entropy, equation of state, isothermal compressibility, thermal expansion coefficient, heat capacities at constant volume and constant pressure, etc., of a Lennard–Jones fluid. The proposed expressions combine accuracy with simplicity and they are valid over the entire supercritical region. The number of simulated states was 265, covering a range of temperatures $T = (1.3\text{–}2.6)$ and densities from $\rho = (0.1\text{–}0.844)$ (both in reduced units). The given number of states permits us to fit the computer simulation data by the corresponding analytical expressions with a total guarantee of confidence.

Because the heat capacity at constant pressure is related to the other quantities, such as the internal energy (through the heat capacity at constant volume) and to the equation of state (through the isothermal compressibility and the thermal expansion coefficient), in testing the goodness of our analytical relations we compared our C_p values with other theoretical values taken from the literature, and found excellent agreement. We also compared our C_p results with experimental data for argon, using our own recently proposed Lennard–Jones intermolecular parameters. Good agreement was again found. © 1997 Elsevier Science B.V.

Keywords: Molecular dynamics; Supercritical simple fluids; Thermodynamic properties; Weeks–Chandler–Andersen theory

1. Introduction

Accurate, simple and reliable expressions to determine the thermodynamical behaviour of a system as a function of the thermodynamic state (T, ρ) and over the entire phase plane had long been a goal pursued by theoretical physicists and chemical engineers. However, the global thermodynamics of a given system is described with complicated and long expressions [1–3]. This involves: firstly, laborious work in their mathematical handling; and secondly, that other thermodynamic properties obtained from standard relations – usually containing derivatives – are seriously affected because of the amplification of the errors. This is the case, for example, when we have a relatively accurate expression to determine the Helmholtz free energy (HFE). The errors of its first derivative, such as the internal energy and the pressure (or equation of state, EOS) are extraordinarily amplified, making the application of this EOS useless in local

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*Corresponding author.

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regions of the phase plane, such as in the determination of the vapour–liquid equilibrium (VLE) curve. Of course, this amplification is more pronounced when we work with the second derivatives of the HFE, such as the heat capacities, isothermal compressibility, thermal expansion coefficient, etc.

Previous work made by our research group [4,5] was devoted to studying the vapour and liquid regions, such as the VLE of simple fluids; the present one is devoted to an extensive study of the supercritical fluid zone, i.e. states above the critical point. There is an increasing interest in the study of supercritical fluids (SCFs) – with intermediate properties between the liquids and gases – because they have application in industry, e.g. the petrochemical, environmental and food industries. For example, in the environmental sector, the SCFs (ethylene, propane, carbon dioxide, etc.) are used to eliminate dangerous waste products by means of the supercritical extraction process.

Despite our being interested in the study of thermodynamics of a simple SCF – as the Lennard–Jones one – the mathematical models proposed in this paper will be taken as reference, and these will be modified and adapted to pre-cited real SCFs in a near future. It is organized as follows: Section 2 treats the Helmholtz free energy (HFE) of this supercritical region. In Section 3, we propose the analytical expressions that give the thermodynamics, of a Lennard–Jones (LJ) system as function of the thermodynamic state. Section 4 tests the goodness of our analytical expressions by means of a comparison between theoretical and experimental results. Finally, Section 5 presents the most important conclusions.

2. The Weeks–Chandler–Andersen theory and the Helmholtz free energy

The Weeks–Chandler–Andersen (WCA) [6] theory of fluids has been a successful tool for investigating the thermodynamic properties of these systems. Thus, many papers have been devoted to studying the most important implications of this theory in both three-dimensional (3D) and two-dimensional (2D) cases (see, e.g. Rull et al. [7], Cuadros et al. [8], Cuadros et al. [9], Cuadros and Mulero [10–12]). The principal advantage of using the WCA theory to predict the thermodynamics of fluids is that the intermolecular forces can be separated into repulsive and attractive parts, such as those suggested by van der Waals (vdW) [8,13]. This permits one to follow the effect of the intensity of the attractive forces in the calculation of the thermodynamic properties of fluids [5,9,14]. For LJ systems, the WCA separation of the intermolecular potential is

$$u_{\mathrm{LJ}}(r) = u_0(r) + \lambda u_{\mathrm{p}}(r), \tag{1}$$

where $u_{\mathrm{LJ}}(r)$ is the well-known (LJ) interaction potential, and $u_0(r)$ and $u_{\mathrm{p}}(r)$ are the repulsive and attractive parts of this potential, respectively.

$$u_0(r) = \begin{cases} u_{\mathrm{LJ}}(r) + 1 & r \le r_{\mathrm{m}} = 2^{1/6} \\ 0, & r > r_{\mathrm{m}} \end{cases} \tag{2}$$

and

$$u_{\mathrm{p}}(r) = \begin{cases} -1 & r \le r_{\mathrm{m}}, \\ u_{\mathrm{LJ}}(r), & r > r_{\mathrm{m}} \end{cases} \tag{3}$$

In the Eqs. (2) and (3), r_{m} is the minimum of the potential, i.e. the distance at which the force changes from repulsive to attractive, and λ a perturbative parameter providing the different contribution or intensity of the intermolecular attractive forces in calculating the thermodynamic properties. When $\lambda = 1$, we have the full LJ potential. In Eqs. (1)–(3), and the following equations, all the properties are expressed in reduced LJ units.

Similar approaches based in other separations of the intermolecular forces have been used to decribe the thermodynamic behaviour of simple fluids (see, e.g. Ref. [15] and references therein).

From the WCA theory and making use of some statistical mechanics arguments, the excess with respect to the ideal gas of the Helmholtz free energy (HFE) per particle has the exact expression [6]:

$$A = A_0 + \rho\alpha_\lambda(T, \rho), \tag{4}$$

where A_0 is the HFE excess of the so-called reference system (molecular interaction due only to the repulsive part, $u_0(r)$, i.e. $\lambda = 0$). The quantity A_0 is given by the Carnahan–Starling equation [4,5,9,16]

$$A_0 = T\frac{4y - 3y^2}{(1-y)^3}, \tag{5}$$

where

$$y = \frac{\pi}{6}\rho d^3 \tag{6}$$

and d is the hard sphere (HS) equivalent diameter, given by the Verlet–Weis [17] criterion

$$d = \frac{0.3837T + 1.068}{0.4293T + 1}. \tag{7}$$

In previous papers [4,18], we have shown that combined Eqs. (5)–(7) give a good picture of the reference system properties.

The function $\alpha_\lambda(T, \rho)$, that gives the contribution of the intermolecular attractive forces to the HFE, is given by [19]

Table 1
Values of $\alpha(T, \rho)$ obtained from MD results of the RDF for the supercritical region, with asymptotic contribution from Eq. (9)

T	ρ	α	T	ρ	α	T	ρ	α	T	ρ	α	T	ρ	α	T	ρ	α
1.3	0.100	6.154	1.5	0.750	7.533	1.8	0.200	6.389	2.0	0.550	7.169	2.2	0.700	7.420	2.4	0.825	7.546
	0.125	6.194		0.800	7.602		0.250	6.506		0.600	7.263		0.750	7.485		0.844	7.566
	0.150	6.305		0.825	7.629		0.300	6.630		0.650	7.352		0.800	7.542	2.5	0.100	6.130
	0.550	7.196		0.844	7.652		0.350	6.741		0.700	7.426		0.825	7.560		0.125	6.195
	0.600	7.300	1.6	0.100	6.072		0.400	6.860		0.750	7.497		0.844	7.583		0.150	6.262
	0.650	7.391		0.125	6.142		0.450	6.966		0.800	7.557	2.3	0.100	6.107		0.200	6.376
	0.700	7.480		0.150	6.295		0.500	7.070		0.825	7.580		0.125	6.203		0.250	6.501
	0.750	7.559		0.200	6.391		0.550	7.178		0.844	7.599		0.150	6.252		0.300	6.632
	0.800	7.623		0.250	6.485		0.600	7.271	2.1	0.100	6.131		0.200	6.398		0.350	6.734
	0.825	7.656		0.300	6.628		0.650	7.361		0.125	6.232		0.250	6.516		0.400	6.856
	0.844	7.671		0.350	6.762		0.700	7.444		0.150	6.241		0.300	6.633		0.450	6.949
1.4	0.100	6.054		0.400	6.862		0.750	7.515		0.200	6.396		0.350	6.725		0.500	7.054
	0.125	6.179		0.450	6.968		0.800	7.577		0.250	6.509		0.400	6.845		0.550	7.156
	0.150	6.259		0.500	7.073		0.825	7.599		0.300	6.605		0.450	6.956		0.600	7.242
	0.200	6.400		0.550	7.176		0.844	7.617		0.350	6.733		0.500	7.056		0.650	7.323
	0.250	6.508		0.600	7.280	1.9	0.100	6.151		0.400	6.849		0.550	7.164		0.700	7.397
	0.300	6.627		0.650	7.372		0.125	6.172		0.450	6.959		0.600	7.250		0.750	7.463
	0.350	6.763		0.700	7.457		0.150	6.233		0.500	7.065		0.650	7.336		0.800	7.518
	0.400	6.870		0.750	7.533		0.200	6.396		0.550	7.168		0.700	7.412		0.825	7.540
	0.450	6.978		0.800	7.593		0.250	6.535		0.600	7.263		0.750	7.479		0.844	7.556
	0.500	7.090		0.825	7.619		0.300	6.621		0.650	7.347		0.800	7.535	2.6	0.100	6.118
	0.550	7.189		0.844	7.636		0.350	6.749		0.700	7.423		0.825	7.553		0.125	6.203
	0.600	7.290	1.7	0.100	6.121		0.400	6.868		0.750	7.490		0.844	7.575		0.150	6.270
	0.650	7.388		0.125	6.192		0.450	6.960		0.800	7.550	2.4	0.100	6.107		0.200	6.376
	0.700	7.472		0.150	6.254		0.500	7.072		0.825	7.573		0.125	6.161		0.250	6.502
	0.750	7.549		0.200	6.386		0.550	7.173		0.844	7.594		0.150	6.268		0.300	6.627
	0.800	7.611		0.250	6.535		0.600	7.262	2.2	0.100	6.109		0.200	6.370		0.350	6.742
	0.825	7.642		0.300	6.635		0.650	7.352		0.125	6.138		0.250	6.501		0.400	6.854
	0.844	7.662		0.350	6.745		0.700	7.436		0.150	6.272		0.300	6.622		0.450	6.947
1.5	0.100	6.084		0.400	6.853		0.750	7.504		0.200	6.377		0.350	6.735		0.500	7.056
	0.125	6.138		0.450	6.962		0.800	7.564		0.250	6.488		0.400	6.851		0.550	7.153
	0.150	6.240		0.500	7.070		0.825	7.592		0.300	6.608		0.450	6.961		0.600	7.242
	0.200	6.381		0.550	7.178		0.844	7.611		0.350	6.732		0.500	7.059		0.650	7.320
	0.250	6.515		0.600	7.280	2.0	0.100	6.124		0.400	6.839		0.550	7.155		0.700	7.390
	0.300	6.663		0.650	7.367		0.125	6.207		0.450	6.952		0.600	7.243		0.750	7.456
	0.350	6.746		0.700	7.447		0.150	6.257		0.500	7.057		0.650	7.332		0.800	7.509
	0.400	6.852		0.750	7.520		0.200	6.380		0.550	7.159		0.700	7.407		0.825	7.532
	0.450	6.979		0.800	7.582		0.250	6.524		0.600	7.254		0.750	7.470		0.844	7.541
	0.500	7.083		0.825	7.607		0.300	6.621		0.650	7.340		0.800	7.525		—	—
	0.550	7.187		0.844	7.628		0.350	6.732									
	0.600	7.287	1.8	0.100	6.133		0.400	6.846									
	0.650	7.376		0.125	6.172		0.450	6.956									
	0.700	7.462		0.150	6.262		0.500	7.066									

$$-\alpha_\lambda(T,\rho) = 2\pi\int_0^\infty r^2 u_\mathrm{p}(r) g_0(r)\mathrm{d}r + 2\pi\int_0^1 \mathrm{d}\lambda \int_0^\infty r^2 u_\mathrm{p}(r)[g_\lambda(r) - g_0(r)]\mathrm{d}r. \qquad (8)$$

Note that $u_\mathrm{p}(r)$ is the attractive part of the intermolecular LJ potential. Here, $g_\lambda(r)$ is the radial distribution function (RDF) of the system when the molecules interact with the potential given by Eq. (1), and $g_0(r)$ is the RDF of the reference system ($\lambda = 0$).

In order to obtain an analytical expression for the $\alpha_\lambda(T,\rho)$ function, we carried out extensive computer simulations over a wide range of densities and temperatures, using the molecular dynamics (MD) method. The RDF data for five values of the perturbative parameter ($\lambda = 0$, 0.25, 0.50, 0.75 and 1) were introduced into the integrals, and then the integrals solved for each thermodynamic state. The results were fitted with an analytical expression for $\alpha_\lambda(T,\rho)$, following the procedure already described in previous papers [9,10,12].

On the other hand, if one wants to obtain valid and useful analytical expressions of the HFE, of its first derivatives (EOS, internal energy, etc.), of its second derivatives (heat capacity, isothermal compressibility, etc.), and so on, for chemical engineering applications, one needs to make the $\alpha_\lambda(T,\rho)$ fit as accurately as possible, not only globally but locally – for each thermodynamic state. Thus, in order to obtain very good global fits of the HFE and/or EOS – even containing a great number of adjustable parameter – there is no assurance of arriving at good expressions for the second derivatives of the HFE, heat capacity, isothermal compressibility, etc. Of course, if one is interested in an expression for the HFE alone, a coarser fit can be tolerated. Another important requirement in technical applications is the simplicity of the analytical model. The simplicity of our model is guaranteed because the $\alpha_\lambda(T,\rho)$ function is linear in density and cubic in temperature. This fact will be reflected in the EOS where, as we will see, the proposed EOS is a vdW-type one, and it has the same structural form as that in previous works [4,5].

For the supercritical fluid region study, we have used the $\alpha(T,\rho)$ (with $\lambda = 1$) values shown in Table 1, obtained from MD results for the RDF. As we can see, the range of temperatures from $T = 1.3$–2.6 and densities from $\rho = 0.1$–0.844 (265 states in total) covered is sufficiently wide range to ensure a good fit. We would like to enphasize that the values of $\alpha(T,\rho)$ shown in Table 1 take into account the asymptotic contribution (AC) because of the truncation of the LJ potential at distance $r_\mathrm{c} = 2.5$. The contribution is [4]

$$\mathrm{AC} = \frac{8}{9}\pi\lambda\left[\left(\frac{1}{r_\mathrm{c}}\right)^9 - 3\left(\frac{1}{r_\mathrm{c}}\right)^3\right]. \qquad (9)$$

The result is the following expression for $\alpha(T,\rho)$:

$$\alpha(T,\rho) = (5.709 + 0.360T - 0.158T^2 + 0.025T^3) + (2.347 - 0.179T - 0.002T^2 + 0.004T^3)\rho, \qquad (10)$$

The percentage mean deviation, when the calculated $\alpha(T,\rho)$ values (Eq. (10)) are compared with the simulation ones, is less than 1%. This equation will be used to obtain other thermodynamic properties in the supercritical fluid region.

3. Thermodynamic properties of LJ fluids as a function of the thermodynamic state

Starting from Eq. (4), and using standard thermodynamic relations, we were able to determine other thermodynamic properties as a function of temperature and density. These thermodynamic properties are: the internal energy, U, entropy, S, pressure, P, isothermal compressibility, χ_T, thermal expansion coefficient, α_e, and heat capacities at constant volume, C_v, and at constant pressure, C_p.

As is well known, χ_T, α_e and C_p are easier properties to determine experimentally than U, C_v, and, of course, S. These properties are related as follows [20]:

$$C_p - C_v = \frac{Tv\alpha_e^2}{\chi_T}, \qquad (11)$$

with T being the temperature, $v = 1/\rho$ the molar volume, and where

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v, \tag{12}$$

is the molar heat capacity at constant volume, obtained directly from the internal energy equation. The thermal expansion coefficient,

$$\alpha_e = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P, \tag{13}$$

and the isothermal compressibility,

$$\chi_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \tag{14}$$

can be obtained, as we noted above, from the EOS.

The internal energy, EOS and entropy are obtained from the following thermodynamic relations:

$$U = A - T\left(\frac{\partial A}{\partial T}\right)_v, \tag{15}$$

$$P = \rho^2\left(\frac{\partial A}{\partial \rho}\right)_T, \tag{16}$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_v. \tag{17}$$

As we can see, Eqs. (15)–(17) contain the first derivatives of the HFE, whereas the quantities such as C_p, C_v, α_e and χ_T are obtained through the second derivatives. Finally, the analytical expressions for all these properties, taking into account Eqs. (4) and (10), are:

excess of the HFE,

$$A(T,\rho) = A_0(T,\rho) - \rho(C_1(T) + \rho C_2(T) + C_3), \tag{18}$$

excess of the internal energy,

$$U(T,\rho) = U_0(T,\rho) - \rho(C_1(T) + \rho C_2(T) + C_3) + \rho T(C_1'(T) + \rho C_2'(T)),$$

entropy,

$$S(T,\rho) = S_0(T,\rho) - \rho(C_1'(T) + \rho C_2'(T)), \tag{20}$$

pressure (EOS),

$$P(T,\rho) = P_0(T,\rho) - \rho^2(C_1(T) + \rho C_2(T) + C_4) - \rho^3 C_2(T), \tag{21}$$

isothermal compressibility,

$$\chi_T = \left(\rho\left(\frac{\partial P_0}{\partial \rho}\right)_T - 2\rho C_1(T) - 6\rho^3 C_2(T) - 2\rho^2 C_4\right)^{-1},$$

thermal expansion coefficient,

$$\alpha_e = \frac{(\partial P_0/\partial T)_\rho - \rho^2 C_1'(T) - 2\rho^3 C_2'(T)}{\rho(\partial P_0/\partial \rho)_T - 2\rho^2 C_1(T) - 6\rho^3 C_2(T) - 2\rho^2 C_4}, \tag{23}$$

molar heat capacity at constant volume,

$$C_v(T,\rho) = 3/2 + (\partial E_0/\partial T)_\rho + \rho T(C_1''(T) + \rho C_2''(T)), \tag{24}$$

where E_0 is the potential energy per particle of the reference system whose parameters are defined in Table 2, and finally, the molar heat capacity at

Table 2
Definition of the parameters involved in Eqs. (18)–(24)

$$A_0(T,\rho) = T\frac{4y-3y^2}{(1-y)^2}$$

$$U_0(T,\rho) = 2T\frac{4y-3y^2}{(1-y)^2} + 6T^2\frac{1}{\mathrm{d}(T)}\left(\frac{\partial \mathrm{d}(T)}{\partial T}\right)_v\frac{2y-y^2}{(1-y)^3}$$

$$S_0(T,\rho) = -\frac{4y-3y^2}{(1-y)^2} - 6T\frac{1}{\mathrm{d}(T)}\left(\frac{\partial \mathrm{d}(T)}{\partial T}\right)_v\frac{2y-y^2}{(1-y)^3}$$

$$P_0(T,\rho) = \rho T\frac{1+y+y^2-y^3}{(1-y)^3}$$

$$E_0(T,\rho) = -6T^2\frac{1}{\mathrm{d}(T)}\left(\frac{\partial \mathrm{d}(T)}{\partial T}\right)_v\frac{2y-y^2}{(1-y)^3}$$

$$C_1(T) = 5.7087 + 0.3602T - 0.1578T^2 + 0.0249T^3$$

$$C_2(T) = 2.3475 - 0.1787T - 0.0017T^2 + 0.0037T^3$$

$$C_3 = 0.5354343$$

$$C_4 = 0.5339657$$

$$C_1'(T) = \left(\frac{\partial C_1(T)}{\partial T}\right)_\rho$$

$$C_2'(T) = \left(\frac{\partial C_2(T)}{\partial T}\right)_\rho$$

$$C_1''(T) = \left(\frac{\partial^2 C_1(T)}{\partial T^2}\right)_\rho$$

$$C_2''(T) = \left(\frac{\partial^2 C_2(T)}{\partial T^2}\right)_\rho$$

constant pressure,

$$C_p(T,\rho) = 5/2 + (\partial E_0/\partial T)_\rho + \rho T(C_1''(T) + \rho C_2''(T)) + Tv\alpha_e^2/\chi_T, \tag{25}$$

where we have made use of Eq. (11).

Eqs. (18)–(25) give the analytical expressions for determining the thermodynamics of LJ fluids as a function of the thermodynamic state. The meaning of the symbols in these equations are listed in Table 2.

4. Comparison with theoretical and experimental results

The results obtained using Eqs. (18)–(25) were compared with theoretical and experimental results. When the HFE data were compared with theoretical values [2], a good agreement was found (mean deviation < 10%) despite our simple HFE equation (the HFE equation of Johnson et al. contains 32 parameters). Also, when our EOS (Eq. (21)) was tested against other EOS [2], a good agreement was again found. On comparing our results of internal energy (Eq. (19)) with other published theoretical results [2], the agreement was good once again (mean deviation ≤5%). Fig. 1 shows the differences (ΔX), between our values obtained from Eqs. (18),(19) and (21), respectively, and similar values obtained by Johnson et al. for one temperature ($T = 1.9$). The goodness of the entropy can be tested through the results for C_v, because this thermodynamic property is related to the entropy by

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_v. \tag{26}$$

The comparison of the C_v data obtained from Eq. (24) with other published [1,21] results again showed good agreement.

Another theoretical test was made for C_v and the expression (Eq. (24)), in the neighbourhood of the critical point. For temperatures near the critical point, the C_v of fluids satisfies the proportionality [22]

$$C_v \propto |T - T_c|^{\alpha_c}, \tag{27}$$

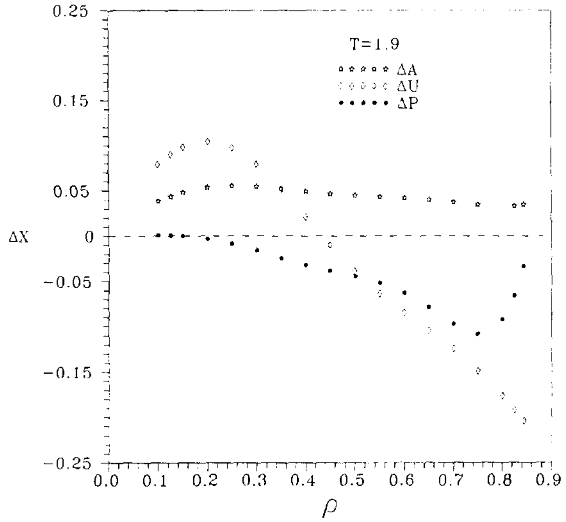

Fig. 1. Differences (ΔX) vs. density, between our results and those obtained from reference [2] for Helmholtz free energy, A, internal energy, U, and EOS, respectively.

T_c being the critical temperature and α_c (written with the subscript 'c' to distinguish it from the $\alpha(T,\rho)$ function and from the thermal expansion coefficient α_e) an exponent that, in the critical region, equals −0.1. Table 3 lists $\ln C_v$ and $\ln(T - T_c)$, as well as values of the critical exponent, α_c, given by

$$\alpha_c = \lim_{T\to T_c^+} \frac{\ln C_v}{\ln|T - T_c|}. \tag{28}$$

One can see that when $T_c = 1.27$ and $\rho_c = 0.35$ then $\alpha_c \simeq -0.1$. Again these values of the critical point are in accordance with others obtained from more complicated statistical mechanics theories [22–25]. For example, the critical point of LJ system reported by Lotfi et al. is $T_c = 1.31$ and $\rho_c = 0.31$. So the relative

Table 3
Critical behaviour of C_v (Eq. (24))

T	ρ	$\ln C_v$	$\ln(T - T_c)$	α_c
1.271	0.35	0.5786	−6.9077	−0.08
1.272	—	0.5786	−6.2146	−0.09
1.273	—	0.5787	−5.8091	−0.10
1.274	—	0.5787	−5.5215	−0.10
1.275	—	0.5787	−5.2983	−0.10
1.276	—	0.5787	−5.1160	−0.11
1.277	—	0.5788	−4.9618	−0.11
1.278	—	0.5788	−4.8283	−0.12
1.279	—	0.5788	−4.7105	−0.12
1.280	—	0.5789	−4.6052	−0.12
1.281	—	0.5789	−4.5100	−0.13

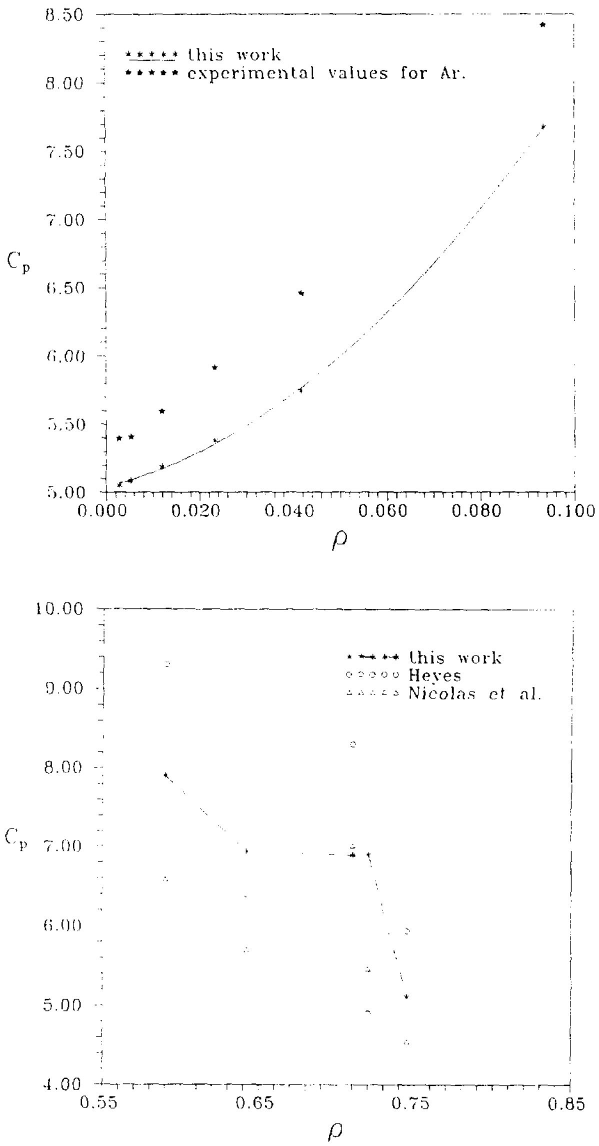

Fig. 2. Plots of C_p vs. density: (a) (*) – curve from our Eq. (25), experimental results from Ref. [24]; (b) dotted line from Eq. (25), (○) – theoretical values from Ref. [21], and (△) – from Ref. [1].

deviation between these values and those proposed by us are -3.15% for T_c and 11.4% for ρ_c.

Since the relation between C_p and C_v (Eq. (11)) involves four of the thermodynamic properties studied here, we think that the comparison of our C_p expression (Eq. (25)) with other published theoretical and experimental results appears to be the most complete that is possible, because agreement between C_p values implies that the expressions for the C_v (or S), α_e and χ_T must also be good (at least, excepting a very improbable fortuitous cancellation of errors). Fig. 2(a) and (b) show the comparison between our C_p expression and other theoretical C_p data [1,21] as well as with experimental data for argon [26]. Two comments must be made with reference to the comparison between our C_p data and the experimental ones. First, the connection between the two sets of data for Ar was made using our own recently published LJ parameters [27] which are $\sigma = 3.623$ Å, and $\epsilon/k = 111.84$ K. Second, the available C_p experimental data for argon refer to the gas region ($T = (0.7493–1.2071)$ and $\rho = (0.0029–0.0934)$ [26], hence, for the comparison, we extrapolated our C_p expression – valid for the supercritical region – to the gas region. This comparison therefore permits us only to estimate the behaviour of the C_p. Nevertheless, the agreement between the two sets of results was very good.

5. Conclusions

We have proposed analytical expressions to give the thermodynamic behaviour of LJ fluids. These expressions were obtained by taking into account the WCA theory of fluids by fitting MD results over a wide range of temperatures and densities. The proposed expressions combine accuracy with simplicity, thus permitting a straightforward and reliable use in chemical engineering and theoretical applications. Despite their mathematical simplicity, the comparison of our thermodynamic expressions with other published theoretical and experimental results appears to be very good. In particular, the expression for the calculation of C_v has an excellent behaviour in the critical region when it is compared with modern theories of the critical point. The C_p expression, obtained from combining the C_v, α_e and χ_T expressions, supports very well its comparison with theoretical and experimental values of C_p, implying that our C_p expression is very good. Finally, we would like to indicate that all these results will be used in the near future in further investigations.

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References

[1] J.J. Nicolas, K.E. Gubbins, W.B. Streett and D.J. Tildesley, Mol. Phys., 37 (1979) 1429.

[2] J.K. Johnson, J.A. Zollweg and K.E. Gubbins, Mol. Phys., 78 (1993) 591.

[3] J. Kolafa and I. Nezbeda, Fluid Phase Equilibria, 100 (1994) 1.

[4] F. Cuadros, W. Ahumada and A. Mulero, Thermochim. Acta, 277 (1996) 85.

[5] F. Cuadros, W. Okrasinski and A. Sanfeld, J. Chem. Phys., 104(14) (1996) 5594.

[6] J.D. Weeks, D. Chandler and H.C. Andersen, J. Chem. Phys., 54 (1971) 5237; 55 (1971) 5422.

[7] L.F. Rull, F. Cuadros and J.J. Morales, Phys. Rev. A, 30 (1984) 2781.

[8] F. Cuadros, A. Mulero and P. Rubio, J. Chem. Educ., 71 (1993) 956.

[9] F. Cuadros, W. Ahumada and A. Mulero, Chem. Phys., 204 (1996) 41.

[10] F. Cuadros and A. Mulero, Chem. Phys., 156 (1991) 33.

[11] F. Cuadros and A. Mulero, Chem. Phys., 160 (1992) 375.

[12] F. Cuadros and A. Mulero, Chem. Phys., 177 (1993) 53.

[13] J.D. van der Waals, Doctoral thesis, (1873), University of Leiden, Amsterdam.

[14] F. Cuadros, W. Okrasinski and A. Mulero, Physica A, 223 (1996) 321.

[15] C.P. Bokis and M.C. Donohue, J. Phys. Chem., 99 (1995) 12655.

[16] N.F. Carnahan and K.E. Starling, J. Chem. Phys., 51 (1969) 635.

[17] L. Verlet and J.J. Weis, Phys. Rev. A, 5 (1972) 939.

[18] F. Cuadros, J.O. Valderrama and A. Mulero , Chem. Engng. Sci., 48 (1993) 513.

[19] J.D. Weeks and J.Q. Broughton, J. Chem. Phys., 78 (1983) 4197.

[20] H.B. Callen, Thermodynamics, A.C. Madrid (Ed.), (1981), Spanish edition.

[21] D.M. Heyes, Chem. Phys., 82 (1983) 285.

[22] R.B. Griffiths, Thermodynamics and Statistical Physics, M.G. Velarde and F. Cuadros (Eds.), Teaching Modern Physics, Singapore: World Scientific, 1995.

[23] H.C. Hansen and Y.R. McDonald, Theory of Simple Liquids, New York, Academic Press, 1976.

[24] A. Lotfi, J. Vrabec and J. Fischer, Mol. Phys., 76 (1992) 1319.

[25] B. Smit, J. Chem. Phys., 96 (1992) 8639.

[26] DIPPD (Design Institute for Physical Property Data) American Institute of Chemical Engineers, 1993.

[27] F. Cuadros, A. Mulero, I. Cachadina and W. Ahumada, Int. Rev. Phys. Chem., 14 (1995) 205.