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Theoretical calculations of the zisothermal compressibility for simple fluids

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Abstract

Nineteen equations of state for hard-sphere fluids and six for Lennard-Jones fluids are reviewed from the literature, and used to calculate the isothermal compressibility. We show that the choice of which equation of state to use to calculate the isothermal compressibility of hard-spheres is most difficult for high densities. We also performed the hard-sphere calculation by using available numerical values of the radial distribution function, finding adequate results only at low densities. Moreover, two recently proposed analytical models that reproduce these radial distribution function values seem not to be valid for the calculation of the isothermal compressibility.

For the Lennard-Jones system, we found first that the influence of attractive intermolecular forces is not negligible at any density; second, that the equations of state lead to different results for states near the phase transitions; third, that none of the equations of state considered here gave values for the isothermal compressibility in full agreement with the available computer simulation results for states near the vapour–liquid coexistence curve; finally, that there was good agreement with available experimental values for liquid argon. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

A great number of analytical expressions, i.e. equations of state (EOSs), giving the compressibility factor of simple fluids, such as the hard-sphere and the Lennard-Jones fluids, can be found in the literature, e.g. [1–8]. Generally, the parameters needed in these EOSs are calculated from fitting computer simulation data for the pressure and/or potential energy. Nevertheless, for analytical expressions to be adequate they must also give good values for other thermodynamic properties. Here we have chosen the isothermal compressibility and try to analyse the results obtained with different EOSs. Our choice is based on the fact that this property is directly related to the pressure and also to the molecular structure as follows.

As is well known, the isothermal compressibility, χ_T, is defined as

$$\chi_T = \frac{1}{\rho}\left[\frac{\partial \rho}{\partial P}\right]_T, \tag{1}$$

where ρ, P and T are density, pressure, and temperature, respectively, and where all properties are expressed in reduced Lennard-Jones (LJ) units. Another way to calculate the isothermal compressi-

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bility is through the statistical mechanics equation [9]:

$$\chi_T = \frac{1}{\rho T}\left[1 + 4\pi\rho\int_0^{0\to\infty}(g(r)-1)r^2\,\mathrm{d}r\right], \tag{2}$$

where $g(r)$ is the radial distribution function, RDF, of the system, r being the intermolecular distance.

To obtain an analytical expression for χ_T from Eq. (1), one requires the dependence of P on density, i.e. an analytical expression for the equation of state. Although a certain number of EOSs have been proposed for the hard-sphere, HS, and Lennard-Jones, LJ, systems, until now the isothermal compressibility has been calculated only for HS systems and using the simplest EOSs as an example in reviews [10] and books [9].

More than 20 analytical expressions for the HS EOS have been published and some reviews of the numerous papers in the literature are available [4,11–14]. Generally, the accuracy of the different EOSs has been studied by comparison with available computer simulation results for the compressibility factor or pressure. No comparison of results obtained for χ_T with each of these analytical expressions has been made, so that the choice of the most appropriate expression may be a difficult task for researchers, especially for calculations where a knowledge of this property is needed [8].

Many of the above mentioned equations can be used to accurately describe the Weeks–Chandler–Andersen (WCA) [15] reference system (only Lennard-Jones repulsive forces) through a scaling procedure [6,14]. In this case, comparison of different results is more difficult, because now the pressure is both density and temperature dependent.

In the case of a Lennard-Jones fluid, there are at least four different accurate expressions for the calculation of the compressibility factor [2,3,16,17], but results for the isothermal compressibility obtained from these expressions have not been published or compared until now. Also we have proposed simpler expressions for the EOS of LJ fluids [6–8] that reproduce with accuracy our computer simulation results for the pressure and potential energy, yield adequate values of the vapour pressure for methane, and give an estimate of the behaviour of the heat capacity at constant pressure of methane and argon.

To obtain numerical or analytical values of χ_T from the RDF using Eq. (2), one needs computer simulation results, solutions of integral equations, or analytical models that fit these results. The accuracy of the data and models has a great influence on the calculation of the isothermal compressibility. Thus, a central statistical mechanics problem is to develop RDF models that yield the same equation of state as when the virial or compressibility equations are used, arriving at a thermodynamically consistent structure [18,19]. For example, when Eq. (2) is used, an analytical expression for the HS χ_T can be obtained from the analytical expression for the RDF obtained by using Percus-Yevick, PY, theory [20]. However, this expression is not thermodynamically consistent with that obtained from the compressibility factor in the PY integral equation [19]. Here we shall consider the numerical results obtained from the self-consistent approximation [9], and also two recently proposed analytical models that reproduce these numerical results [21].

Glandt and Fitts [22] have calculated the isothermal compressibility for two-dimensional LJ fluids by using the $g(r)$ obtained from the solution of the PY equation, and by using the EOS obtained from the differentiation of the compressibility pressure equation. They found that the differences are small except at low temperatures, where $g(r)$ is long-ranged. In the present work, the calculation of χ_T from the RDF of three-dimensional LJ fluids is not considered, because no adequate data for $g(r)$ at great distances could be found.

The paper is organised as follows. In Section 2 we present the EOS and RDF models for HS systems and give results for the isothermal compressibility obtained with them. In Section 3 the LJ system is considered: first, the EOS of LJ fluids are presented, and then the isothermal compressibility is calculated for both the WCA reference system and the LJ system. Comparison with experimental results is made in Section 4. Conclusions are presented in Section 5.

2. The hard-sphere system

As is well known, the hard-sphere (HS) system is defined by an interaction potential considering only the repulsive forces between the molecules. The HS system exhibits several simplifying features which make it a convenient starting point for the calculation of properties of dense fluids, especially at high temperatures where the HS EOS is a good approximation to describe the properties of real fluids [9]. For this system, only the knowledge of the value of the RDF at the point of contact, $g_{\mathrm{HS}}(r{=}1)$, is needed to calculate the thermodynamical properties. The value of $g_{\mathrm{HS}}(r{=}1)$ can be expressed analytically, giving an equation of state such as the well-known Carnahan–Starling EOS [1]. This and other EOSs proposed in the literature are presented in Section 2.1.

When the statistical mechanics Eq. (2) is used to calculate χ_T, the value of $g_{\mathrm{HS}}(r)$ is needed for all values of r. These values are available from approximate theories, such as the Percus-Yevick or self-consistent approximation theories [23], from computer simulation results [24,25] and from analytical models [19,21,26,27].

As is well known, the PY theory works well at low and moderate densities but fails at high densities, particularly in the liquid state. On the other hand, the expression given by Verlet and Weis [26] is not completely analytical because it includes the RDF obtained from the PY equation, and that RDF does not have a parametric expression. Finally, the model given by Bravo-Yuste et al. [18,19], which provides a RDF that is thermodynamically consistent with a given EOS, is not simple in form, and includes only the range $1.0173 \leq r \leq 2.2727$, and the integral of Eq. (2) can be calculated only over a small range.

Here we shall consider 19 analytical expressions for the EOS, and also the $g_{\mathrm{HS}}(r)$ obtained from numerical results of the self-consistent approximation for $r \leq 5$ [23], and from the analytical expressions proposed by Valderrama and Faúndez [21]. We investigate the discrepancy between the results obtained with each EOS and with numerical data and the Valderrama–Faúndez models, as well as the thermodynamic consistency in the calculation of χ_T.

2.1. Equations of state for hard-spheres

Many of the existing analytical expressions for the EOS of HS systems have been proposed on the basis of theoretical considerations or by directly fitting computer simulation data and/or a number of virial coefficients. The use of different computer simulation results and the consideration of several analytical forms for the equations have led to a wide range of proposals. In this work we consider the 19 analytical expressions for the compressibility factor, $Z{=}P/(\rho T)$, shown in Table 1 in chronological order, Eqs. (3)–(21), and as a function of the packing fraction:

$$\eta = \pi\rho d^3/6, \tag{22}$$

d being the molecular diameter, e.g. $d{=}1$ in the case of the HS system, or as a function of the density ratio between the volume occupied by the spheres and the total volume:

$$\xi = \frac{\rho}{\sqrt{2}}. \tag{23}$$

As an attempt to classify the EOSs in terms of complexity we shall consider as "simple" expressions those in which the denominator has the form $(1-\eta)^n$. The simplest expression is that derived from the scaled particle theory (SPT) [28], Eq. (3), which is the same as the one derived from the Percus-Yevick compressibility equation. Another very simple expression is that derived by Thiele [20] from the Percus-Yevick virial equation (PYT), Eq. (4). The expression given by Carnahan and Starling (CS) [1], Eq. (6), has been widely used in empirical and theoretical equations to describe the repulsive contributions to Z in real or model systems [5–8,29,30]. Expressions proposed by Kolafa (quoted by Boublik [11]), Eq. (11), and by Baus and Colot [12], Eqs. (12) and (13) which we denote as BC4 and BC6 in Table 1, are similar to CS, although they have a better accuracy in reproducing the virial coefficients. Maeso et al. [13] and Solana [31] improved and generalised the Carnahan–Starling method [1] to obtain EOSs for HS fluids in d-dimensions, their proposal being shown in Eqs. (14), (16) and (17), respectively. These equations are aimed at reproducing computer simulation results at low and at metastable densities.

We also consider "complex" expressions, in which the denominator includes a more complicated polynomial. We include here the proposals of Ree and Hoover [32], Eq. (5), which reproduce the theoretical values of the virial coefficients up to the fifth, and of Hall [33], Eq. (7), which is an empirical modification of CS. A third proposal is that of Erpenbeck and Wood [34], Eq. (10), which fits their own computer simulation data. Finally, we include the Padé approximant proposed by Sánchez [35], Eq. (18).

Table 1
Analytical expressions for the compressibility factor, $Z=P/(\rho T)$, or equation of state (EOS) for hard-spheres

Reiss et al. [28]	$Z_{\mathrm{SPT}} = (1+\eta+\eta^2)/(1-\eta)^3$(Scaled Particle Theory)	(3)
Thiele [20]	$Z_{\mathrm{PYT}} = (1+2\eta+3\eta^2)/(1-\eta)^2$(Percus-Yevick Theory)	(4)
Ree–Hoover [32]	$Z_{\mathrm{RH}} = (1+1.75399\eta+2.31704\eta^2+1.108928\eta^3)/(1-2.246004\eta+1.301056\eta^2)$	(5)
Carnahan–Starling [1]	$Z_{\mathrm{CS}} = (1+\eta+\eta^2-\eta^3)/(1-\eta)^3$	(6)
Hall [33]	$Z_{\mathrm{H}} = (1+\eta+\eta^2-0.67825\eta^3-\eta^4-0.5\eta^5-1.7\eta^6)/(1-3\eta+3\eta^2-1.04305\eta^3)$	(7)
Le Fevre [36]	$Z_{\mathrm{LF}} = (1-0.8824\eta)/((1-1.5708\eta)(1+1.0232\eta)(1-2.9552\eta+2.5521\eta^2)(1-1.3795\eta+2.1339\eta^2))$	(8)
Andrews [37]	$Z_{\mathrm{A}} = (5.1834\xi/(1-1.5340\xi+0.5340\xi^2))-(1.3504/\xi)\ln(1-0.7405\xi)-(4.8534/\xi)\ln(1-1.5340\xi+0.5340\xi^2)-(15.977/\xi)\ln((1-0.5340\xi)/(1-\xi))$	(9)
Erpenbeck–Wood [34]	$Z_{\mathrm{EW}} = (1+1.7227128\eta+2.2532688\eta^2+0.89244864\eta^3-0.3430292\eta^4)/(1-2.2772872\eta+1.32624176\eta^2)$	(10)
Boublik [11]	$Z_{\mathrm{K}} = (1+\eta+\eta^2-(2/3)(\eta^3+\eta^4))/(1-\eta)^3$	(11)
Baus–Colot [12]	$Z_{\mathrm{BC4}} = (1+\eta+\eta^2-0.6352\eta^3-0.8697\eta^4)/(1-\eta)^3$	(12)
Baus–Colot [12]	$Z_{\mathrm{BC6}} = (1+\eta+\eta^2-0.6352\eta^3-0.8697\eta^4+0.2543\eta^5+2.9231\eta^6)/(1-\eta)^3$	(13)
Maeso et al. [13]	$Z_{\mathrm{MSAV1}} = (1+2\eta+3\eta^2+2.364799\eta^3+1.494402\eta^4+1.750397\eta^5+4.672003\eta^6)/(1-\eta)^2$	(14)
Maeso et al. [13]	$Z_{\mathrm{MSAV2}} = (1+20.15439\eta+18.09291\eta^2+31.55595\eta^3)/((1+19.15439\eta-2.061472\eta^2+15.09823\eta^3)(1-\eta)^3)$	(15)
Solana [31]	$Z_{\mathrm{SOL1}} = (1+\eta+\eta^2-0.6352\eta^3)/(1-\eta)^3$	(16)
Solana [31]	$Z_{\mathrm{SOL2}} = (1-\eta-1.6352\eta^3+1.4005\eta^4+1.1764\eta^5)/(1-\eta)^5$	(17)
Sánchez [35]	$Z_{S} = (1+1.024385\eta+1.104537\eta^2-0.4611472\eta^3-0.7430382\eta^4)/(1-2.975615\eta+3.007000\eta^2-1.097758\eta^3)$	(18)
Wang et al. [4]	$Z_{\mathrm{W1}} = \sum_{i=1} A_i\xi^{i-1}/(1-\xi)^2$(see Table 2)	(19)
Wang et al. [4]	$Z_{\mathrm{W2}} = \sum_{i=1} B_i\xi^{i-1}/(1-\xi)^3$(see Table 2)	(20)
Wang et al. [4]	$Z_{W3} = (1/\xi)\sum_{i=1} C_i(\xi/(1-\xi))^i$(see Table 2)	(21)

The packing fraction, η, and the density ratio, ξ, are defined in Eqs. (22) and (23), respectively. Coefficients for Eqs. (19)–(21) are given in Table 2.

Table 2
Coefficients for the EOSs for hard-spheres proposed by Wang et al. [4], Eqs. (19)–(21)

A_1	1.00000
A_2	0.96192
A_3	0.55927
A_4	−0.54794
A_5	−0.94405
A_6	−0.64773
A_7	−0.00006
A_8	−5.13137
A_9	0.30736
A_{10}	7.45126
B_1	1.00000
B_2	−0.03808
B_3	−0.40265
B_4	−1.10721
B_5	−0.39611
B_6	0.29632
B_7	0.64715
B_8	−2.37792
B_9	0.75175
B_{10}	2.83837
C_1	1.00000
C_2	1.96192
C_3	0.55927
C_4	−1.10721
C_5	0.55626
C_6	−0.11923
C_7	0.00954

We shall also consider some more complex expressions: first, that proposed by Le Fevre [36], Eq. (8); second, Andrews' expression [37], Eq. (9), which would perhaps be considered the most complex because it contains logarithmic terms; third, a second proposal of Maeso et al. [13], Eq. (15).

Finally, we include the most recent proposals of Wang et al. [4], which should be labelled as somewhere intermediate between "simple" and "complex", since they use a different variable and a new analytical form. The three analytical expressions proposed by Wang et al. [4], Eqs. (19)–(21) with coefficients A_i, B_i and C_i given in Table 2, are the only ones that give the real behaviour of the HS system in the close-packed limit ($Z \rightarrow \infty$, for $\rho = \rho_c = \sqrt{2}$).

An important difference between these EOSs is the location of poles (values of the density or η where Z becomes infinite and χ_T is zero). As was observed by Thiele [20], "simple" equations must fail at densities close to the closest packing ($\eta_c \approx 0.7405$), since their singularity ($\eta = 1$) corresponds to the density $\rho \sim 1.91$ at which the whole space would be filled. The "complex" equation has a pole at regular or random close-packing [13], whereas Wang et al. have a singularity at the correct close-packing limit ($\xi = 1$).

2.2. RDF data and models

As was mentioned above, we use here numerical values of the RDF for the HS systems obtained from the self-consistent approximation [23]. Results are available in the range $0.1 \leq \rho \leq 0.8$ and for $r \leq 5$, including the contact value $g_{\mathrm{HS}}(r=1)$.

Recently Valderrama and Faúndez [21] have studied the validity of a model for the $g_{\mathrm{HS}}(r)$ proposed by Matteoli and Mansoori [38], which is a combination of rational, exponential and trigonometrical functions and has only four parameters:

$$g_{\mathrm{MM}}(r) = 1 + \frac{(a-c)}{r^b} + \frac{(r-1+c)}{r} \exp[-d(r-1)]\cos[(e(r-1)], \quad (24)$$

where the parameter $a = (g(r=1) - 1)$ is fixed to give the exact location and value of the first maximum of the RDF, and b, c, d, e, are adjustable parameters for each density. Valderrama and Faúndez [21] proposed a modification of the Matteoli–Mansoori model to improve its accuracy, as follows:

$$g_{\mathrm{VF}}(r) = 1 + \frac{a}{r^{2.4a+4.425}} + \left[\frac{r-1}{r}\right]^b \exp[-c(r-1)]\cos[d(r-1)], \quad (25)$$

where only three coefficients are calculated (b, c, d). Valderrama and Faúndez [21] have obtained these parameters by fitting the numerical values obtained in the self-consistent approximation [23] for each density. These authors conclude that their model is significantly better for $\rho = 0.1$ and of similar accuracy for other densities.

Models given by Eqs. (24) and (25) have not been used until now in the calculation of thermodynamical properties. Obviously, in the case of the compressibility factor, the models give the same result as the self-consistent approximation, which reproduces the Carnahan and Starling [1] values with mean deviation of 1.3% for the range $0.1 \leq \rho \leq 0.8$, the maximum deviation being 2% for $\rho = 0.4$.

2.3. Results

2.3.1. Isothermal compressibility from the EOS

The isothermal compressibility for the HS system was calculated by using Eq. (1) and the 19 EOSs presented in Table 1[39]. Table 3 lists the values of (χ_T T) obtained by using the CS equation, Eq. (6), which is the most used and best known expression, for densities in the stable region $0.1 \leq \rho \leq 0.943$ [40], and in the metastable region $0.95 \leq \rho \leq 1.07$ [41]. For the close-packed density ($\rho_c \approx 1.4142$) χ_T must be equal to zero, because P goes to infinity, so that this value is also included in Tables 3 and 4 for the CS and the other EOSs, respectively, as a test of their accuracy in this density limit. Table 4 also gives the mean deviation between the isothermal compressibility calculated by using the other 18 EOSs with respect to that obtained from the CS, for different ranges of densities. As was shown by us [14,39], the CS equation gives adequate values of the pressure for hard-spheres except in the range $0.885 < \rho < 0.943$, where W3 gives the best accuracy.

Table 3
Values for (χ_T T) of hard-spheres obtained from the Carnahan and Starling [1] equation (Eq. (6) in Table 1)

ρ	$\chi_T\ T$
0.1	6.6110
0.2	2.2027
0.3	0.9828
0.4	0.4935
0.5	0.2634
0.6	0.1453
0.7	0.0814
0.8	0.0457
0.82	0.0407
0.84	0.0362
0.844	0.0354
0.86	0.0323
0.88	0.0287
0.90	0.0255
0.92	0.0226
0.94	0.0201
0.943	0.0197
0.95	0.0189
0.97	0.0167
1.0	0.0139
1.07	0.0089
1.4142	6.6×10^{-3}

For low densities, $\rho < 0.6$, only the SPT and PYT expressions, Eqs. (3) and (4), lead to large deviation. In this range the Kolafa EOS, Eq. (11), is the most accurate in the case of the pressure [14], and, as can be seen in Table 4, the mean deviation between the Kolafa and the CS expressions for χ_T is very small here (0.19%).

For $0.6 \leq \rho \leq 0.8$ the SPT, PYT and W3 expressions, Eqs. (3), (4) and (21) respectively, give the greatest deviations from the CS results. These equations also give large discrepancies in the calculation of the pressure with respect to the computer simulation values [14]. Seven EOSs give mean deviations (MD) between 1% and 3%, whereas the remaining eight give MD less than 1%, the smallest corresponding to the Hall and BC4 expressions, Eqs. (7) and (12), respectively.

For the highest stable densities, $0.8 < \rho \leq 0.943$, there are greater differences between the results obtained with the various EOSs, with only seven expressions giving mean deviations less than 2% with respect to the CS results. For this region, the accuracy of the CS equation is questionable because of the poor results found for the pressure [39]. Better results for the pressure might be obtained using other expressions, such as W3, Eq. (21).

For the metastable region, $0.943 < \rho \leq 1.07$, the Erpenbeck–Wood, Kolafa and Maeso et al. expressions, Eqs. (10), (11) and (15), lead to results which are similar to the CS case, which is accurate for the calculation of pressure in this range [39]. MDs greater than 10% are found for five EOSs, including W3. The only conclusion that can be drawn for this region is that there is a great variability in the results, so that the choice of which expression is most appropriate is difficult.

The above results show therefore, that for both the stable and metastable ranges of hard-sphere fluids, the use of Eqs. (10), (11) and (15) give practically the same results (mean deviations less than 1% for all densities ranges) for the isothermal compressibility as when the simpler CS expression is considered. The use of more complex expressions is thus only justified in the case of the higher densities.

Bravo-Yuste et al. [19] have pointed out that the χ_T calculated from Sanchez's equation, $(\chi_T)_{\mathrm{S}}$, is greater than $(\chi_T)_{\mathrm{SPT}}$ in the stable and metastable regions. Moreover, they indicate that the two values are prac-

Table 4
Mean deviations between the isothermal compressibility for hard-spheres calculated by using the EOSs shown in Table 1 and that obtained with the CS equation

EOSs	MD (%)				$\chi_T\, T$
	$0.1\leq\rho<0.6$	$0.6\leq\rho\leq0.8$	$0.8<\rho\leq0.943$	$0.943<\rho\leq1.07$	$\rho_c=\sqrt{2}$
SPT	1.17	6.02	9.45	11.86	5.21×10^{-4}
PYT	−2.49	−14.91	−15.39	−37.06	1.46×10^{-3}
RH	0.15	−0.49	−2.39	−5.20	1.26×10^{-3}
H	0.16	0.11	0.54	3.17	4.51×10^{-12}
LF	0.20	−0.94	−3.89	5.36	1.13×10^{-2}
A	−0.17	1.44	6.31	13.87	-6.67×10^{-13}
EW	0.32	0.56	0.04	−0.94	9.78×10^{-4}
K	0.19	0.25	−0.24	−0.87	7.00×10^{-4}
BC4	0.16	−0.12	−1.06	−2.12	7.29×10^{-4}
BC6	0.25	1.73	4.00	6.69	4.89×10^{-4}
M1	0.22	0.68	0.49	−0.26	7.81×10^{-4}
M2	0.20	0.62	0.79	0.95	6.48×10^{-4}
Sol1	0.43	2.29	3.67	4.68	6.03×10^{-4}
Sol2	0.21	1.58	5.13	11.37	1.84×10^{-4}
S	0.20	1.10	3.42	8.27	1.50×10^{-7}
W1	0.06	−2.08	−1.82	9.88	9.39×10^{-17}
W2	0.13	−2.86	−4.05	7.48	1.44×10^{-21}
W3	−0.26	−4.76	−4.13	12.03	5.83×10^{-40}

The value of ($\chi_T\, T$) at the close-packed density is also shown.

tically equal for $\rho\approx1.07$, i.e. at the density associated with the glass transition [41]. Also $(\chi_T)_\mathrm{S}$ is less than $(\chi_T)_\mathrm{SPT}$ for higher densities. Following these authors, this means that the appearance of a different structure in the system can be predicted theoretically and that the method proposed by them will not be applicable to Sanchez's equation beyond the stable or metastable fluid regions. None of the other expressions considered here gives the same value as $(\chi_T)_\mathrm{SPT}$ for $\rho\approx1.07$. For example, $(\chi_T)_\mathrm{W3}$ is some 18% less than $(\chi_T)_\mathrm{SPT}$ at that density.

Finally, as can be seen in Tables 3 and 4, most of the EOSs give small but finite values of χ_T at the close-packed density, the W3 value being the nearest to zero.

2.3.2. Isothermal compressibility from the RDF

We consider now the calculation of the isothermal compressibility from RDF data and models. Table 5 shows values of ($\chi_T\, T$) obtained from Eq. (2) by using numerical values for the RDF of the self-consistent approximation [23], by using the Matteoli–Mansoori model [38], Eq. (24), and by using the Valderrama–Faúndez model, Eq. (25), with the parameters giving in [21]. In all the cases the integral of Eq. (2) was calculated only from $r=1$ to $r=5$, because in the range from $r=0$ to $r=1$ the RDF is exactly zero with a contribution to ($\chi_T\, T$) of $[1-4\pi/3]/\rho$, and for $r>5$ the approximation $g(r)=1$ can be made so that there is no contribution to the isothermal compressibility.

The discrepancy between the three sets of results indicates the sensitivity of the compressibility equation to the use of numerical or analytical approximations, especially for high densities where the RDF is long-ranged and the assumption that $g(r)=1$ for $r>5$ seems not to be valid [22].

Table 5
Values of ($\chi_T\, T$) for hard-spheres obtained by using numerical data of the radial distribution function given by the self-consistent (SC) approximation [23], and by using the Matteoli–Mansoori and the Valderrama–Faúndez models, Eqs. (24) and (25)

ρ	SC	MM	VF
0.1	6.611	7.113	6.725
0.2	2.204	2.384	2.398
0.3	0.985	1.433	1.201
0.4	0.441	1.134	0.809
0.5	0.271	0.926	0.663
0.6	0.125	0.798	0.675
0.7	0.081	0.756	0.783
0.8	0.140	0.543	0.712

The values of Table 5 can be compared with those obtained from the CS equation, given in Table 3. As one can see, the two models, although valid for the calculation of $g(r)$, seem not to be valid for the calculation of the isothermal compressibility (except perhaps if Eq. (25) is used for $\rho=0.1$). In fact, a deviation of 0.9% for the Valderrama–Faúndez model with respect to the $g(r)$ values of the self-consistent approximation leads to a deviation of nearly 22% in the calculation of the isothermal compressibility. On the other hand, the agreement between the numerical self-consistent approximation and the Carnahan–Starling expression is excellent for low densities ($\rho<0.4$), and good (deviations near 10%) for intermediate densities ($0.4\leq\rho\leq0.6$). For high densities the self-consistent approximation and the analytical models considered here seem to be "inconsistent" due to the truncation of the RDF data.

These results indicate that it is very difficult to obtain a self-consistent and simple analytical or numerical model for the RDF, with only other more complex models, such as that proposed by Bravo-Yuste et al. [19] for HS fluids, being available until now.

3. The Lennard-Jones system

The Lennard-Jones system is defined by the so-called LJ 12-6 potential, which is strongly repulsive for short distances ($r\leq2^{1/6}$) and weakly attractive for larger distances, and which has been widely used as a model of real fluids [2,3,5–9,16,17,42]. Here we shall consider the calculation of the isothermal compressibility for the LJ liquid from different expressions for its equation of state.

3.1. Equations of state

Three of the most successful EOSs are that of Nicolas et al. [16], that of Adachi et al. [17] and that of Johnson et al. [2], which have the same analytical expression:

$$\begin{aligned}P = {}&\rho T + C_1\rho^2 + C_2\rho^3 + C_3\rho^4 + C_4\rho^5 + C_5\rho^6\\ &+ C_6\rho^7 + C_7\rho^8 + C_8\rho^9 + (D_1\rho^3 + D_2\rho^5\\ &+ D_3\rho^7 + D_4\rho^9 + D_5\rho^{11} + D_6\rho^{13})\exp(-3\rho^2),\end{aligned}\tag{26}$$

where

$$\begin{gathered}C_1 = x_1T + x_2T^{1/2} + x_3 + x_4T^{-1} + x_5T^{-2}\\ C_2 = x_6T + x_7 + x_8T^{-1} + x_9T^{-2}\\ C_3 = x_{10}T + x_{11} + x_{12}T^{-1}\\ C_4 = x_{13}\\ C_5 = x_{14}T^{-1} + x_{15}T^{-2}\\ C_6 = x_{16}T^{-1}\\ C_7 = x_{17}T^{-1} + x_{18}T^{-2}\\ C_8 = x_{19}T^{-2}\\ D_1 = x_{20}T^{-2} + x_{21}T^{-3}\\ D_2 = x_{22}T^{-2} + x_{23}T^{-4}\\ D_3 = x_{24}T^{-2} + x_{25}T^{-3}\\ D_4 = x_{26}T^{-2} + x_{27}T^{-4}\\ D_5 = x_{28}T^{-2} + x_{29}T^{-3}\\ D_6 = x_{30}T^{-2} + x_{31}T^{-3} + x_{32}T^{-4}\end{gathered}\tag{27}$$

the x^i being constant coefficients calculated by fitting computer simulation results. Nicolas et al. [16] calculated these coefficients by fitting results for the pressure and potential energy in the density range $0\leq\rho\leq1.2$ and for temperatures from 0.5 to 6.0 (the exact temperature range may be different for each density), and by requiring the critical point to be $T_C=1.35$ and $\rho_C=0.35$. Adachi et al. [17] obtained the coefficients x_1 to x_5 from theoretical LJ fluid second virial coefficients, and the other 27 coefficients by fitting pressure results for 800 data points in the range $0<\rho<1.0$ and $0.7<T<3.0$. However, Johnson et al. [2] note that in these early works there were few vapour–liquid equilibrium data, and that the critical point of the LJ fluid is not known accurately. In particular they show that the Nicolas et al. [16] equation does not accurately predict the saturation properties obtained by computer simulations. Thus, Johnson et al. [2] use new computer simulation results for the pressure and potential energy, including some points in the metastable regions for both the vapour–liquid and liquid–solid phase transitions, together with a more accurate estimate of the critical point: $T_C=1.313$ and $\rho_C=0.310$ [42]. As in the Adachi et al. [17] case, the first five coefficients were obtained from the second virial coefficient, and the others from fitting computer simulation results in the range $0<\rho\leq1.25$ and $0.7\leq T<6.0$ (175 different state points).

Despite their accuracy, the above EOSs present two main problems: a lack of theoretical basis, which does not allow one to give a physical meaning to each term and makes it difficult to apply them over different ranges or for different systems, and their complicated analytical form, which makes them very difficult to handle mathematically in order to obtain other thermodynamic properties.

Another class of EOS consists of semi-theoretical expressions, which have a theoretical basis but still contain some adjustable parameters [3,5,7,8]. In these EOSs, the traditional idea of van der Waals or of the more recent Weeks et al. (WCA) [15] theory, i.e. the separation of the repulsive and attractive contributions to the thermodynamical properties, forms the theoretical basics. The repulsive contribution of LJ potential is modelled thorough the EOS of a HS system, which is modified by using a temperature-dependent molecular diameter in the calculation of the packing fraction, Eq. (22).

The EOS of Kolafa and Nezbeda (KN) [3] is based on a perturbed virial expansion, where the reference is the K expression, Eq. (11) in Table 1, modified by using the molecular diameter:

$$\begin{aligned} d_{\mathrm{KN}}(T) =& 0.011117524/T - 0.076383859/T^{1/2} \\ &+ 1.080142248 + 0.000693129T^{1/2} \\ &- 0.063920968 \log T. \end{aligned} \tag{28}$$

The proposed analytical equation is then:

$$P_{\mathrm{KN}}/(\rho T) = Z_{\mathrm{K}}(d_{\mathrm{KN}}) + \rho(1 - 2\gamma\rho^2) \exp(-\gamma\rho^2)\beta(T) + \sum jK_{i,j}T^{\,i/2-1}\rho^j, \tag{29}$$

where $K_{i,j}$ are 19 constant coefficients, taking i values from 0 to −4 and j from 2 to 6, γ is another adjustable parameter and $\beta(T)$ is the residual (with respect to the hard-spheres) second virial coefficient, for which KN propose an analytical expression similar to that of the diameter, Eq. (28), i.e.

$$\beta(T) = \sum C_i T^{i/2} + C_{\ln} \log T \tag{30}$$

with C_i being seven constant coefficients (for i=0, −2, −3, −4, −5, −6, −7) and $C_{\ln}$ an additional coefficient. The coefficients (27 in all) are calculated by fitting computer simulation results for pressure, potential energy and chemical potential (when available) over the same range as in the Johnson et al. [2] case but adding some new results and data for T=10. Kolafa and Nezbeda [3] pointed out that their EOS is significantly more accurate and has fewer parameters that previous proposals.

The EOS proposed by us in previous works [5,7,8], which we called the "CM" equation, is based on the separation of the LJ potential proposed in the Weeks et al. [15] Theory. Thus, the pressure of the LJ system can be expressed as

$$P_{\mathrm{CM}} = P_{\mathrm{R}} - P_{\mathrm{At}}, \tag{31}$$

where P_{R} is the pressure of the WCA reference system (only repulsive forces), and P_{At} is the pressure obtained when only the attractive forces are considered.

In previous works [6,14,39] we have shown that the WCA reference system can be described by using an HS EOS where the packing fraction, η, is calculated by using a temperature-dependent expression for the molecular diameter in Eq. (22). In particular, we have considered recently [14] two different analytical expressions for this diameter: that given by Kolafa and Nezbeda [3], Eq. (28), and the simpler form given by Verlet and Weis [26]:

$$d_{\mathrm{VW}}(T) = (0.3837T + 1.068)/(0.4293T + 1). \tag{32}$$

We note that expressions for d_{VW} and d_{KN} give practically the same results, with there being only a small deviation at high temperatures. However, their derivatives with respect to the temperature, which must be used in the calculation of the potential energy for example, are different, especially for low temperatures.

In that previous work, we recommended the use of the W3 expression, Eq. (21), together with d_{VW}, Eq. (32), to calculate the compressibility factor of the WCA reference system when wide ranges of temperature and density are considered. None of the other expressions for the HS system must be used at low temperatures and high densities if accuracy is required. When only low or intermediate densities ($\rho \leq 0.65$) are considered, most simple equations such as the well-known CS equation can be used with success. For this reason, and because the difference between $(\chi_T)_{\mathrm{CS}}$ and $(\chi_T)_{\mathrm{W3}}$ is greater than between other expressions (except for the SPT and PYT, Eqs. (3) and (4)) for $0.6 \leq \rho \leq 0.8$, Table 4, we shall consider here both the CS and W3 expressions, modified with the VW diameter, to calculate the contribution of the repulsive forces to the isothermal compressibility of the LJ system. The use of the KN diameter gives practically the same results.

In the CM expression, Eq. (31), the attractive contribution to the pressure is introduced, for liquid states, as follows [5,7]:

$$\begin{aligned} P_{\mathrm{At}} = {}& \rho^2(8.774 - 4.675T + 2.388T^2 - 0.391T^3) \\ & + \rho^3(-1.725 + 5.352T - 2.795T^2 \\ & + 0.458T^3). \end{aligned} \tag{33}$$

The analytical form of P_{At} is then very much simpler than the earlier ones, being cubic in the density (as is the van der Waals expressions) and in the temperature, and containing only eight constant coefficients.

3.2. Isothermal compressibility

Our aim in this work is to analyse the results for the isothermal compressibility obtained from these different EOSs for LJ systems, and also to compare these results with others obtained from computer simulations or from experiments. In the case of the CM semi-theoretical expression, based on the WCA theory, the contribution of the repulsive and attractive forces to the isothermal compressibility can be quantified. All calculations were made in the liquid range T=0.7–1.3 and $0.45 \leq \rho \leq 0.844$ (see Table 6).

As starting point, it is interesting to analyse the differences between using the CS and the W3 expressions, Eqs. (6) and (21), respectively, to calculate the isothermal compressibility of the WCA reference system, because they have different accuracy over each density range for the HS system. Note that now the product ($\chi_T\, T$) is temperature dependent, i.e. for the WCA reference system the isothermal compressibility is not linear with respect to the temperature, as was the case for the HS system. In particular, we found that while for the HS system, the CS results for χ_T are greater than the W3 results for all the stable densities, in the case of the WCA reference system the W3 values are always greater than the CS ones. As is shown in Table 6, for states near the triple (T=0.7, ρ=0.844) or the critical (T=1.313, ρ=0.31) points the difference is always less than 5%, whereas for the other liquid states the differences are from 5% to 7%. These results indicate that the choice of either the W3 or the CS expressions leads to different results for the total isothermal compressibility over most of the liquid range.

In order to analyse the contribution of repulsive and attractive forces, we note that the CM expression for the isothermal compressibility can be expressed as follows:

$$(\chi_T)_{\mathrm{CM}} = \frac{1}{(1/(\chi_T)_{\mathrm{R}}) + (1/(\chi_T)_{\mathrm{At}})}, \tag{34}$$

where $(\chi_T)_{\mathrm{R}}$ is calculated from P_{R}, and $(\chi_T)_{\mathrm{At}}$ is obtained from the P_{At} analytical expression given by Eq. (33).

Table 6 shows how in the liquid range the contribution of the repulsive forces, $(\chi_T)_{\mathrm{R}}$, is always positive and decreases when the temperature or density increases, taking reduced values of from 0.02 at the triple point, to 0.27 near the critical point. The contribution $(\chi_T)_{\mathrm{At}}$ is always negative and also decreases in absolute value when the density increases, being practically independent of temperature. It takes values from −0.06 to −0.27. The complete isothermal compressibility decreases when the temperature or the density increases, taking values from 0.04 to 13.6. Thus $(\chi_T)_{\mathrm{R}}$, calculated with the CS or the W3 expressions, always represents less than 61% of the value of χ_T. Near the critical point this contribution is less than 10%. The contribution of the attractive forces must therefore always be taken into account, especially near the critical point. Here, we conclude that the WCA reference system is not a sufficiently good approximation to calculate the isothermal compressibility of LJ liquids.

As a second step, we investigated whether the different EOSs lead to very different or to equal values of the isothermal compressibility for LJ liquids. For that, we calculated the values of χ_T by using Nicolas et al.'s [16], Adachi et al.'s [17], Johnson et al.'s (J) [2] and Kolafa and Nezbeda's (KN) [3] EOSs, as well as our CM [5,7] expressions. In particular, we considered here two EOSs based on the CM expression, Eqs. (31)–(33). In the first we use the CS EOS, Eq. (6), for the repulsive part, and in the second we use the W3 EOS, Eq. (21). The two expressions are then denoted by CSCM and W3CM, respectively (Tables 6 and 8).

Table 6
Values of the isothermal compressibility for some liquid LJ states obtained by using EOSs proposed by the authors

ρ	T	$(\chi_T)_{\mathrm{R}}$		$(\chi_T)_{\mathrm{At}}$	$(\chi_T)_{\mathrm{LJ}}$	
		CS	W3	CM	CSCM	W3CM
0.45	1.3	0.2675	0.2693	−0.2747	10.2241	13.6185
0.50	1.3	0.1958	0.1981	−0.2170	2.0020	2.2673
0.55	1.3	0.1444	0.1471	−0.1750	0.8264	0.9226
0.60	1.2	0.1133	0.1166	−0.1442	0.5289	0.6087
0.60	1.3	0.1072	0.1101	−0.1436	0.4221	0.4722
0.65	1.2	0.0841	0.0876	−0.1201	0.2810	0.3229
0.65	1.3	0.0798	0.0829	−0.1196	0.2398	0.2702
0.70	1.1	0.0662	0.0698	−0.1021	0.1880	0.2206
0.70	1.2	0.0626	0.0659	−0.1013	0.1639	0.1888
0.70	1.3	0.0595	0.0626	−0.1008	0.1454	0.1651
0.75	1.0	0.0520	0.0555	−0.0883	0.1269	0.1498
0.75	1.1	0.0491	0.0523	−0.0872	0.1125	0.1310
0.75	1.2	0.0466	0.0496	−0.0864	0.1012	0.1165
0.75	1.3	0.0444	0.0472	−0.0859	0.0920	0.1049
0.80	0.8	0.0439	0.0467	−0.0794	0.0980	0.1132
0.80	0.9	0.0409	0.0436	−0.0775	0.0864	0.0995
0.80	1.0	0.0384	0.0410	−0.0761	0.0776	0.0890
0.80	1.1	0.0364	0.0389	−0.0751	0.0705	0.0806
0.80	1.2	0.0346	0.0370	−0.0743	0.0648	0.0738
0.80	1.3	0.0331	0.0354	−0.0738	0.0600	0.0680
0.825	0.8	0.0375	0.0394	−0.0741	0.0758	0.0842
0.825	0.9	0.0350	0.0370	−0.0723	0.0678	0.0758
0.825	1.0	0.0330	0.0350	−0.0709	0.0616	0.0691
0.825	1.1	0.0313	0.0333	−0.0699	0.0566	0.0635
0.825	1.2	0.0298	0.0318	−0.0692	0.0524	0.0589
0.825	1.3	0.0286	0.0305	−0.0687	0.0489	0.0549
0.844	0.7	0.0359	0.0369	−0.0727	0.0711	0.0748
0.844	0.8	0.0332	0.0344	−0.0704	0.0629	0.0674
0.844	0.9	0.0311	0.0325	−0.0686	0.0568	0.0617
0.844	1.0	0.0293	0.0308	−0.0673	0.0520	0.0570
0.844	1.1	0.0279	0.0294	−0.0663	0.0481	0.0530
0.844	1.2	0.0266	0.0282	−0.0656	0.0448	0.0495
0.844	1.3	0.0255	0.0271	−0.0651	0.0420	0.0465

Contribution of repulsive forces, $(\chi_T)_{\mathrm{R}}$, is calculated by using both the CS and the W3 expressions, Eqs. (6) and (21), together with the Verlet–Weis diameter, Eq. (32). The contribution of attractive forces, $(\chi_T)_{\mathrm{At}}$, is calculated by using the CM expression, Eq. (33).

By comparing results, we found that, as was expected, the maximum deviations occurred for temperatures and densities near the phase transitions. In general, J and KN lead to very similar results over the whole range, except near the critical point where the difference is near 17%. The EOSs proposed by Nicolas et al. [16] and by Adachi et al. [17] give results in good agreement with the previous two only for ρ=0.75 or for the highest temperatures and densities, i.e. far from phase transitions. Values obtained with Nicolas et al.'s EOS are always nearer to the J and KN results than those obtained with Adachi et al.'s EOS, except for states very close to the critical point.

With respect to our CM expressions, we always found differences greater than 5% between the values obtained with the CSCM and with the W3CM equations (Table 6). The CSCM equation gives results in good agreement (deviation less than 5%) with the J and KN values only for states far from phase transitions. On the contrary, only for states near the phase transitions does the use of the W3 expressions instead of the CS one lead to results in better agreement with these obtained with the J or KN equations. Thus for example, for the triple point, T=0.7 and ρ=0.844, the W3CM expression is the only one considered here giving a value for the isothermal compressibility similar to those of the J and KN equations.

In sum, which EOS is chosen to calculate the isothermal compressibility for LJ liquids can lead to very different results near the phase transitions, and especially near the critical point.

Table 7 shows computer simulation results for (χ_T) obtained by Lotfi et al. [42] for a set of T and ρ very near the vapour–liquid curve of the LJ fluid. The uncertainties of the values given in the simulation are also shown, the maximum being 21%. Here, we tried to use the cited EOSs to reproduce these values (within the simulation uncertainties), taking into account that it is near the critical point where the greatest differences between the different EOSs were found.

Our results indicate that none of the EOSs for LJ liquids is in a full agreement with the Lotfi et al. values [42]. In particular, for T=1 and especially for the critical temperature T=1.3, no EOS gives results within the uncertainties of the computer simulation. For these two temperatures only the KN expression, Eq. (29), gives values similar to those of Lotfi et al. The contrary is found for T=1.1, where all the EOSs except KN give good agreement. With respect to the CM equations, the use of the W3 expressions instead of the CS leads to better agreement with Lotfi et al.'s data except for T=0.85–0.95 and T=1.1. In particular, the W3CM expression is the only one that gives good agreement (within the uncertainties of the computer simulation results) for four thermodynamical states (T=0.8, 1.0, 1.05 and 1.25).

Table 7
Values of the isothermal compressibility for states very near to the vapour–liquid curve of LJ fluids, obtained by Lotfi et al. through computer simulation [42]

T	ρ	χ_T	$\Delta\chi_T$ (%)
0.70	0.84257	0.0847	6.5
0.75	0.82138	0.0908	3.5
0.80	0.79887	0.1125	6.7
0.85	0.77553	0.117	9.4
0.90	0.75202	0.154	10.4
0.95	0.72833	0.186	11.3
1.00	0.70179	0.281	5.3
1.05	0.67197	0.369	10.6
1.10	0.6414	0.385	17.9
1.15	0.60557	0.613	16.2
1.20	0.5678	1.05	11.4
1.25	0.5157	2.32	20.7
1.30	0.4259	13.6	2.9

The uncertainties of these values, $\Delta\chi_T$, are also given.

In conclusion, each EOS gives values similar to those of the computer simulation only for certain particular temperatures and densities. Both the accuracy of the computer simulation results of Lotfi et al. [42] and the validity of the EOSs for thermodynamical states very near the vapour–liquid transition could be questioned.

4. Comparison with experimental results

As a final test of the validity of the EOSs, we tried to reproduce experimental values of the isothermal compressibility. We considered the data given by Streett and Staveley [43] for liquid argon in the range 100–140 K and pressures from 50 to 600 atm. Although values of χ_T for some substances near the triple point are available [9,44], they were not considered here because of the lack of accuracy in the determination of the exact triple temperature and density for real substances. Reed and Gubbins [9] have tried to reproduce these values for argon, nitrogen and oxygen by using the scaled particle theory equation, Eq. (3), for HS. However, as they indicate, this equation does not give quantitatively correct values, although it does predict qualitative trends. Here, we consider only the EOSs for LJ fluids.

In order to compare the theoretical and experimental results, the relationship between the properties expressed in reduced LJ units and in real units must be specified. These relationships are:

$$T(K) = \left(\frac{\varepsilon}{k}\right)T, \tag{35}$$

$$\rho\ (\mathrm{mol\,cm^{-3}}) = \frac{\rho}{N_a\sigma^3}, \tag{36}$$

$$\chi_T\ (\mathrm{atm^{-1}}) = \chi_T\frac{\sigma^3 N_a}{(\varepsilon/k)R}, \tag{37}$$

where σ and ε are the LJ parameters, k is Boltzmman's constant, N_a is Avogadro's number and R is the perfect gas constant expressed in atm cm^3 K^{-1} mol^{-1}. For Ar the LJ parameters commonly used are [45–47]:

Table 8
Absolute mean deviations (AMD) for each temperature between the isothermal compressibility calculated by using EOSs for LJ fluids and the experimental results for liquid argon [43]

		AMD (%)					
T (K)	ρ (kmol m^{-3})	Nicolas et al. [16]	Adachi et al. [17]	J [2]	KN [3]	CSCM [5,7]	W3CM (this work)
100	33.3–36.7	3.5	9.4	4.1	4.7	9.5	3.3
105	32.4–36.2	4.3	9.7	5.2	4.7	8.4	3.3
110	31.6–35.7	6.0	8.3	6.3	5.0	8.6	5.9
115	30.7–35.2	7.2	8.9	6.7	5.0	8.7	7.6
120	29.7–34.7	6.2	5.6	6.8	5.5	11.8	3.7
125	28.7–34.2	7.8	9.0	6.2	4.4	9.5	7.4
130	27.6–33.7	8.0	9.2	5.9	4.3	10.5	6.2
135	26.3–33.2	7.9	8.7	6.5	5.2	10.0	4.6
140	24.7–32.7	10.8	12.4	8.9	7.9	13.2	4.6
Total		6.8	9.0	6.2	5.2	10.0	5.2

σ=3.405×10^{-8} cm and (ε/k)=119.8 K, so that the experimental range, expressed in reduced LJ units, is $0.835\leq T\leq 1.17$ and $0.634\leq\rho\leq 0.873$.

Table 8 shows the absolute mean deviation between the isothermal compressibility calculated with each of the EOSs for LJ fluids and the experimental result for each temperature. When the whole range was considered, the last column in Table 8, all the EOSs reproduce the experimental values with deviations less than 10%, KN and our W3CM expressions being the most accurate, and the Adachi et al. [17] and our CSCM expression giving the largest deviations. The Johnson et al. [2] EOS is the most accurate of those expressed by Eq. (26). As expected in this liquid range, the use of the W3 expression leads to better results than the CS expression for all temperatures. Finally, we note that the accuracy was not always the same when different ranges of temperatures were considered. Except with our W3CM equation, the maximum deviations are found at the highest temperature, 140 K. Moreover our W3CM equation gives better accuracy than the KN equation for low and high temperatures.

Finally, it should be noted that Ananth et al. [45] have shown that the anisotropic contributions to the isothermal compressibility are very small for liquids and supercritical fluids, except in the density range $0.25<\rho<0.55$. This means that the good results obtained with liquid argon with the cited EOSs can be extrapolated to other simple liquids such as oxygen, nitrogen or methane.

5. Conclusions

The isothermal compressibility is an important thermodynamic property, which is related to both macroscopic and microscopic properties of fluids. However, theoretical calculations of this property have been restricted to examples in reviews or books. The calculation was made here in order to study the accuracy of different equations of state proposed in the literature for both hard-sphere and Lennard-Jones fluids. In the case of hard-spheres, the calculation was also made by using numerical values and analytical models for the radial distribution function.

For hard-sphere fluids, 19 analytical expressions for the equation of state were considered. Nine of them were considered to be ‘‘simple’’ expressions, another four ‘‘complex’’, another three ‘‘more complex’’, and finally, three had a new analytical form which was proposed recently by Wang et al. [4]. We showed that the simple expression proposed by Carnahan and Starling [1] gave similar results to other simple or complex expressions for both stable and metastable densities. In particular, for the lowest densities all equations gave practically the same results, whereas for intermediate densities the simplest SPT and PYT expressions (Eqs. (3) and (4) in Table 1), together with the more recent W3 expression, Eq. (21), gave the greatest deviations from the CS expression. For the highest stable densities the use of the W3 expression was able to give better results than those obtained with CS. For the metastable region there were great differences between the results, so that the choice of the most appropriate expressions is very difficult. In the close-packed limit, the W3 expression seems to be the most adequate. Finally, we note that, as was pointed out by Bravo-Yuste et al. [19], only the S and SPT expressions gave similar values at the glass transition density.

We also calculated the isothermal compressibility by using numerical data obtained in the self-consistent approximation, and by using recently proposed analytical models for the radial distribution function of hard-spheres. The results varied greatly, especially at high densities, which indicates the sensitivity of the compressibility equation, Eq. (2), to the use of numerical or analytical approximations. The self-consistent approximation gave values that were very similar to those of the CS equation for low densities, with only fairly good agreement for intermediate densities. The disagreement was great for high densities. Finally we showed that the analytical models used here are not valid for calculations of the isothermal compressibility.

Six analytical expressions were used to calculate the isothermal compressibility of Lennard-Jones fluids. Three of them are well-known semi-empirical equations and have the same complex analytical form (Eq. (26)) but different coefficients. The others are semi-theoretical, i.e. they have a theoretical basis. One of them (KN, Eq. (29)) has a complex analytical form, whereas those proposed by the present authors are very simple and are based on the Weeks–Chandler–Andersen separation of the Lennard-Jones potential.

Comparison of the results obtained with each of these EOSs showed that the greatest differences occurred near the phase transitions, and especially near the critical point.

The EOSs based on WCA theory [15], Eq. (31), permit one to study the influence of repulsive and attractive contributions to the isothermal compressibility. Here, we showed that the contribution of the repulsive forces is always less than 61%, and therefore, that the contribution of the attractive forces is not negligible at any density. The WCA reference system does not give a sufficiently good approximation to calculate the isothermal compressibility of LJ liquids. Moreover, whether the CS or the W3 expressions was chosen to calculate the isothermal compressibility of the WCA reference system (only repulsive contributions) led to different results (deviations greater than 5%), especially for densities far from the triple or the critical point.

None of the EOSs used gave values for the isothermal compressibility in full agreement with the computer simulation results of Lotfi et al. [42] for states very near the vapour–liquid coexistence curve: each EOS gave values similar to those of the computer simulation only for certain particular temperatures and densities. Both the accuracy of Lotfi et al.'s computer simulation results and the validity of the EOSs for thermodynamical states very near the vapour–liquid transition could be questioned.

The experimental isothermal compressibility data of liquid argon in the range 100–140 K given by Streett and Staveley [43] can be reproduced with good agreement (absolute mean deviation near 5%) by using the semi-theoretical KN or W3CM equations, and even with the semi-empirical Johnson et al.'s equation [2]. As was concluded by Ananth et al. [45], good results could be obtained with more anisotropic simple fluids. With respect to the equations based on the Cuadros–Mulero expression [5,7], the use of the W3 instead the CS EOS always yielded better results.

Finally, as a general conclusion, we can state that in any thermodynamic modelling process there is an interrelation between the analytical form of the EOS, the property (pressure, isothermal compressibility, vapour pressure, etc.) used for the fit, the region of the phase plane where experimental or computer simulation values of the property under study are available, and the molecular interaction parameters used. Each one influences the other, and it is very difficult to obtain the same coefficients in the EOS model if one uses different properties in the fitting procedure.

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