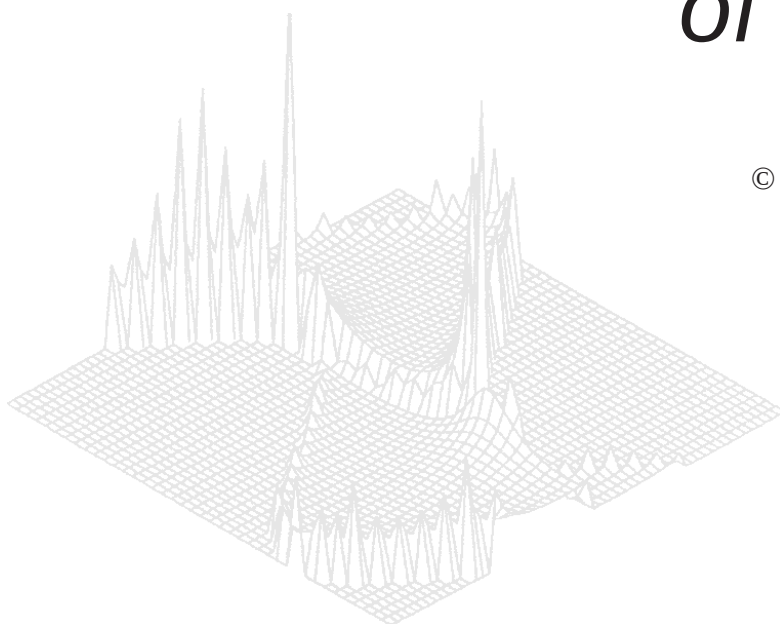

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Vapour–Liquid Equilibrium Properties for Two- and Three-dimensional Lennard-Jones Fluids from Equations of State

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Abstract

Vapour–liquid equilibrium properties for both three- and two-dimensional Lennard-Jones fluids were obtained using simple cubic-in-density equations of state proposed by the authors. Results were compared with those obtained by other workers from computer simulations and also with results given by other more complex semi-theoretical or semi-empirical equations of state. In the three-dimensional case good agreement is found for all properties and all temperatures. In the two-dimensional case only the coexistence densities were compared, producing good agreement for low temperatures only. The present work is the first to give numerical data for the vapour–liquid equilibrium properties of Lennard-Jones fluids calculated from equations of state.

1. Introduction

The knowledge of phase transitions of pure or mixed fluids is essential in many practical applications (Quirke 1996; Toulhoat 1996). Applied physicists and chemists as well as engineers commonly use empirical expressions (Reid *et al.* 1987; Vetere 1986) or purely empirical equations of state (EOSs) (Soave 1972; Peng and Robinson 1976; Patel and Teja 1982; Valderrama 1990; Zabaloy and Vera 1996) that correlate directly with experimental data to a greater or lesser degree of accuracy. Nevertheless, there is no purely empirical expression or EOS that can give accurate results for different properties, for different substances and over the complete temperature and density ranges. Moreover, these expressions do not have a theoretical basis that permits an adequate connection to be made between the intermolecular potential and the phase behaviour. Finally, the application of these EOSs to the evaluation of vapour–liquid equilibrium (VLE) properties is not an easy task numerically, and although some shortcut techniques have been developed, they are not applicable to every EOS (Wisniak *et al.* 1998).

There are also some EOSs for real fluids that have a theoretical basis and include analytical expressions that contain a number of adjustable parameters, specific to each fluid, and which are obtained by reproducing the experimental vapour pressure with greater or lesser precision (Aly and Ashour 1994; Plackov *et al.* 1995). Nevertheless, for these EOSs, the VLE coexistence densities, i.e. the VLE curves, have not been presented by the corresponding authors.

The calculation of phase diagram curves or properties from purely theoretical models is an extremely difficult task, so solutions have been obtained only for

a few important and well-known cases, such as the Lennard-Jones fluids, that can serve as models for some simple fluids (rare gases, methane, etc.). In these theoretical calculations the aim is to predict the VLE properties rather than to fit one or more of them. Theoretical calculations can be made by using perturbation theories (Ananth *et al.* 1974; Carley 1978; Fischer *et al.* 1984; Song and Mason 1989), density functional theories (Fairobent *et al.* 1982; Mederos *et al.* 1985; Curtin and Ashcroft 1986; Mederos *et al.* 1993), integral equations (Duh and Henderson 1996), or through the Born–Green–Yvon equation (Wendland 1997). One needs, however, knowledge of difficult concepts in statistical mechanics and sophisticated mathematical tools. Even then, these approaches do not provide analytical equations that can facilitate their application to practical problems.

Direct molecular simulations of the phase transitions of a given model constitute another tool in current use (Quirke 1996; Toulhoat 1996; Gubbins 1996) but such simulations obviously require extraordinary computational effort and access to adequate computers and software.

Another alternative is the use of EOSs based on a fit to computer simulation results for a given model, such as the Lennard-Jones (LJ) fluid, over a wide range of temperature and densities (Reddy and O'Shea 1986; Johnson *et al.* 1993). Despite their accuracy, there are two main problems with these semi-empirical EOSs: the lack of a theoretical basis, which makes it difficult to apply the EOS over different ranges and/or for different systems, and their complicated analytical form (the Benedict–Webb–Rubin type EOS contains 33 adjustable parameters), which makes their mathematical handling very complicated.

Finally, there are semi-theoretical EOSs (Henderson 1977; Kolafa and Nezbeda 1994), which have a theoretical basis and contain some parameters that can be fitted to reproduce computer simulation results over a wide range of temperatures and densities, including states far from the phase transitions. No data (only figures) of the VLE properties of LJ fluids have been published for either the semi-empirical or semi-theoretical EOSs.

The particular study of two-dimensional (2D) systems is of great interest in research on surface phenomena. Experimental studies on the physical adsorption of fluids (rare gases) onto a solid substrate (graphite) indicate that the adsorbed molecules behave qualitatively in many ways like a 2D fluid that exhibits numerous phase transitions (Fairobent *et al.* 1982). Thus, as we have shown in previous work (Mulero and Cuadros 1997), the study of the 2D LJ fluid is a good starting point towards the goal of reproducing experimental results in adsorption phenomena. A subject of interest, and indeed of some controversy, is the shape of the phase diagram for 2D LJ fluids (Bakker *et al.* 1984; Mederos *et al.* 1985; Singh *et al.* 1990). In particular, the data for the VLE curve has always been determined by using molecular simulations (Singh *et al.* 1990; Smit and Frenkel 1991; Jiang and Gubbins 1995), and there have been no attempts to use EOSs, as proposed by Henderson (1977) or by Reddy and O'Shea (1986). Indeed, we know of only two attempts to study the phase transitions of adsorbed fluids theoretically (Fairobent *et al.* 1982; Jiang and Gubbins 1995).

In order to overcome the difficulties presented by the different approaches, we have proposed semi-theoretical equations for LJ fluids (Mulero and Cuadros 1996; Cuadros *et al.* 1997), which are based on the well-known Weeks–Chandler–Andersen (WCA, 1971) theory, by fitting our computer simulation results obtained over a

wide range of temperatures and densities. The proposed EOSs have a simple analytical form (they are cubic in density, as is, for example, the van der Waals EOS) in both 3D and 2D fluids, and have given good results in the calculation of different properties (Mulero and Cuadros 1996; Cuadros *et al.* 1997). Moreover, these equations can include the perturbative parameter of the WCA theory, and hence can be used for substances in which the attractive or repulsive forces play a greater or lesser role than in the LJ model (Cuadros *et al.* 1996*b*).

The proposed analytical expressions for the EOSs are used in this work in order to obtain the VLE properties for 3D and 2D LJ fluids. Comparison is made with results of computer simulations and of other EOSs proposed in the literature. We note that the main idea is to predict, rather than to fit, the VLE properties, by using EOSs that were not specifically designed to study phase transition properties.

The paper is organised as follows. In Section 2 we present the EOSs used. In Section 3, results for the VLE properties are presented and compared with earlier results obtained from computer simulations and semi-empirical and semi-theoretical equations of state. Finally, the most important conclusions of the work are presented in Section 4.

2. Equations of State for LJ Fluids

The Lennard-Jones fluids are defined by their intermolecular potential:

$$u(r) = 4(r^{-12} - r^{-6}), \quad (1)$$

where r denotes the intermolecular distance. In this paper we shall use only reduced LJ variables, i.e. all properties are expressed and calculated in units of the minimum value of the LJ intermolecular potential, ϵ , and of the distance at which the potential is zero, σ . As is well-known, the use of an effective LJ potential for each real fluid permits the determination of its properties. Also, we note that this model can be used as a first step towards the study of real adsorbed systems. Indeed, Jiang and Gubbins (1995) have shown recently that, because of the large density fluctuations in 2D fluids, the effect of the solid substrate on the coexistence properties is very small. Thus these properties can be calculated for real physisorbed systems by using a 2D LJ model with the adequate effective LJ parameters (Mulero and Cuadros 1997).

There are semi-empirical EOSs that are based solely on the fitting of computer simulation data for the LJ potential, and thus describe at least the pressure and potential energy with relatively good precision. However, as noted in the Introduction, they contain a large number of adjustable parameters and are thus difficult to handle. The Johnson *et al.* (JZG, 1993) and the Reddy and O'Shea (RO, 1986) semi-empirical EOSs are the most accurate for 3D and 2D LJ fluids, respectively. The analytical expression proposed for the reduced pressure (P , in units of σ^n/ϵ , n being the dimension), as a function of the reduced temperature (T , in units of k_B/ϵ , k_B being Boltzman's constant) and of the reduced density (ρ , in units of σ^n), is

$$P = \rho T + C_1 \rho^2 + C_2 \rho^3 + C_3 \rho^4 + C_4 \rho^5 + C_5 \rho^6 + C_6 \rho^7 + C_7 \rho^8 + C_8 \rho^9 \\ + (C_9 \rho^3 + C_{10} \rho^5 + C_{11} \rho^7 + C_{12} \rho^9 + C_{13} \rho^{11} + C_{14} \rho^{13}) \exp(-3\rho^2), \quad (2)$$

where the coefficients C_i are polynomial functions of the temperature, and contain 32 adjustable parameters.

We also consider the semi-theoretical equation of Kolafa and Nezbeda (KN, 1994), which is valid only for 3D LJ fluids, and is based on a perturbed virial expansion. The KN expression for the pressure is

$$P_{\text{KN}}/\rho T = Z_K(d_{\text{KN}}) + \rho(1 - 2\gamma\rho^2)\exp(-\gamma\rho^2)\beta(T) + \sum_{i,j} K_{ij}T^{i/2-1}\rho^j, \quad (3)$$

where Z_K is an analytical expression for the compressibility factor of the reference system (including only contributions from repulsive forces), which is very similar to the well-known Carnahan and Starling (1969) EOS for hard spheres, and which includes an analytical expression for the effective repulsive diameter d_{KN} , with five adjustable coefficients; $\beta(T)$ is the residual (with respect to that of hard spheres) second virial coefficient, for which KN propose a temperature dependence that includes a fractional power of the temperature as well as a logarithmic term:

$$\beta(T) = \sum_i C_i T^{i/2} + C_{\ln} \log T, \quad (4)$$

so that seven coefficients are needed (Kolafa and Nezbeda 1994). The coefficients K_{ij} are constant, where i takes values from 0 to -4 and j from 2 to 6 (19 coefficients in all). Finally, γ is also an adjustable parameter.

In previous work (Mulero and Cuadros 1996; Cuadros *et al.* 1997), we have shown the validity for both 2D and 3D LJ fluids of semi-theoretical EOSs based on WCA theory (Weeks *et al.* 1971) and with simple analytical expressions. In WCA theory, the LJ intermolecular potential (1) is separated into a reference part, which contains all the short-range repulsive forces, and a perturbation part containing all the long-range attractive forces. A perturbative parameter permits a continuous variation from the reference system to the full LJ system.

In WCA theory, the EOS can be written as follows:

$$P(T, \rho) = P_0(T, \rho) - \rho^2 \alpha(T, \rho) - \rho^3 \left(\frac{\partial \alpha(T, \rho)}{\partial \rho} \right), \quad (5)$$

with P_0 being the pressure of the reference system (only repulsive forces), and $\alpha(T, \rho)$ a temperature and density function that represents the contribution of attractive forces and is expressed by Weeks *et al.* (1971) as a double integral. We note here that the validity of WCA theory has been amply verified and the theory widely used (Mulero and Cuadros 1996; Cuadros *et al.* 1996a; Matyushov and Schmid 1996).

To calculate the properties of the reference system, i.e. P_0 , a scaling procedure from the properties of hard sphere (3D case) or disk (2D case) systems must be made. In our EOSs we use the Carnahan and Starling (1969) expression for the 3D LJ reference system,

$$P_0(T, \rho) = \rho T \frac{1 + y + y^2 - y^3}{(1 - y)^3}, \quad (6)$$

and the scaling particle theory expressions for the 2D LJ case,

$$P_0(T, \rho) = \frac{1}{(1 - y)^2}. \quad (7)$$

Here y is the packing fraction

$$y = \pi \rho d(T)^n / 2n, \quad (8)$$

n being the dimension of the system, and $d(T)$ the molecular diameter expression proposed by Verlet and Weis (1972),

$$d = (0.3837T + 1.068) / (0.4293T + 1), \quad (9)$$

which gives practically the same values as the d_{KN} proposed by Kolafa and Nezbeda (1994).

In order to calculate $\alpha(T, \rho)$ in (5), molecular dynamics simulations were carried out for 3D and 2D LJ fluids over a wide range of temperatures and densities (Cuadros *et al.* 1997; Mulero and Cuadros 1996), and the results were then fitted by the analytical expression

$$\alpha(T, \rho) = \sum_{i=0}^5 B_i T^i + \rho \sum_{i=6}^{12} B_i T^{(i-6)}, \quad (10)$$

the coefficients B_i being given in Table 1 for both 2D and 3D cases.

In an earlier work (Cuadros *et al.* 1997), we have shown that the thermodynamic properties of 3D LJ fluids can be accurately calculated by taking different coefficients for $\alpha(T, \rho)$ in the vapour and in the liquid regions of the phase diagram. Here, to describe the coexistence region we use coefficients given in Table 1 and we denote the resulting equation the ‘CM’ EOS.

For 2D LJ fluids we consider here the coefficients given in Table 1, which we recently proposed (Cuadros *et al.* 1997), and which were obtained through a thermodynamic shift from 3D to 2D and are valid for both the vapour and the liquid ranges. This model gives very small deviations in the calculation of pressure at low temperatures, so that a good-quality calculation of the VLE curve must be expected. In this case we denote the resulting EOS by ‘CMO’.

Finally, because our computer simulations were performed with the intermolecular potential truncated at distances $r > 2.5$, the asymptotic contributions to the thermodynamic properties must be added. For the 3D case these asymptotic contributions are included in the coefficients, whereas in 2D, the contributions are $-0.240484\rho^2$ and -0.320777ρ for the pressure and chemical potential, respectively.

Table 1. Coefficients for the CM equation of state (10) for 3D and 2D LJ fluids

	3D		2D
	Vapour	Liquid	
B_0	16.53202	-14.13750	1.57183
B_1	-20.12203	122.09695	2.51944
B_2	15.21162	-282.03559	-2.48617
B_3	-4.12454	320.63715	0.68022
B_4	0	-180.60196	0
B_5	0	40.456090	0
B_6	3313.63909	89.57846	2.73231
B_7	-19583.72760	-491.09891	-5.14467
B_8	48000.27322	1085.86562	4.70071
B_9	-62433.34138	-1189.26565	-1.24911
B_{10}	45433.04423	646.48983	0
B_{11}	-17533.11813	-139.74604	0
B_{12}	2802.89418	0	0

3. Vapour-Liquid Equilibrium Properties

Although there are different methods for determining the VLE curve from EOSs (rectilinear diameters, graphical methods, Maxwell's construction, etc.), the standard thermodynamic procedure requires the equality of the pressure and chemical potential of the vapour phase with their corresponding values in the liquid phase at a given temperature:

$$P(T, \rho_v) = P(T, \rho_l), \quad \mu(T, \rho_v) = \mu(T, \rho_l), \quad (11)$$

where ρ_v and ρ_l are the densities at the liquid and vapour coexistence phases, respectively, and where the expression for the chemical potential, μ , can be obtained directly from the pressure through well-known thermodynamical relations.

As was remarked in the Introduction, computer simulations can be used to obtain the VLE curves directly. Although the simulation methods should guarantee the fulfillment of equation (11), in some cases the values of P or μ at the coexistence densities are not given (Adams 1976; Singh *et al.* 1990; Smit 1992; Jiang and Gubbins 1995). In other cases, when these values are given (Panagiotopoulos *et al.* 1988; Smit and Frenkel 1991; Plackov and Sadus 1997), the associated uncertainties can be very high. In the following sections we therefore first compare the present results with those obtained from different published computer simulations, and then with the results obtained from other EOSs.

(3a) Three-dimensional Lennard-Jones Fluid

We consider here three sets of data for the VLE properties of 3D LJ fluids obtained from computer simulations. First, we examine the results obtained by Panagiotopoulos *et al.* (1988), which have maximum uncertainties of 12.5% and 6.5% for ρ_v and ρ_l , and of 13% and 189% for the vapour and liquid pressures, respectively. Uncertainties in the chemical potentials are not given, but the maximum relative difference between the values of μ_v and μ_l is 2.4%. Second, we note the results obtained by Lotfi *et al.* (1992) in the range $T = 0.7$ – 1.3 , with

maximum uncertainties of 5.6% for ρ_v , 0.5% for ρ_l (except at $T = 1.3$, where the value is 3.5%), 4.6% for the pressure, and 0.7% for the chemical potential. Third, we consider the most recent results of Plackov and Sadus (1997), which are given with maximum uncertainties of 22.7%, 4.9%, and 100% for ρ_v , ρ_l and the pressure, respectively. The maximum relative difference between the values of μ_v and μ_l is 1.4%. In this case, the large uncertainties in the pressure may not be important to the main aim of their work, which is to evaluate the repulsive and attractive contributions to the VLE properties.

From the above analysis, we can conclude that the results of Lotfi *et al.* (1992) are the most accurate for the VLE of 3D LJ fluids, and must therefore be taken as a reference for comparison with other theoretical results.

Recently Duh and Henderson (1996) have reported VLE properties for 3D LJ fluids obtained from a new integral equation theory in the range $T = 0.6\text{--}1.25$ (see Fig. 1). Although the shape of the VLE curve in Fig. 1 is practically the same as that obtained by Lotfi *et al.* (1992), except for the liquid density there are important numerical discrepancies. Thus deviations with respect to the results of Lotfi *et al.* (1992) are less than 7% for ρ_l , from 0.3% to 35% for ρ_v , and from 0.022% to 35.8% for the pressure. The best results of the Duh–Henderson approximation are obtained for temperatures near 1.1.

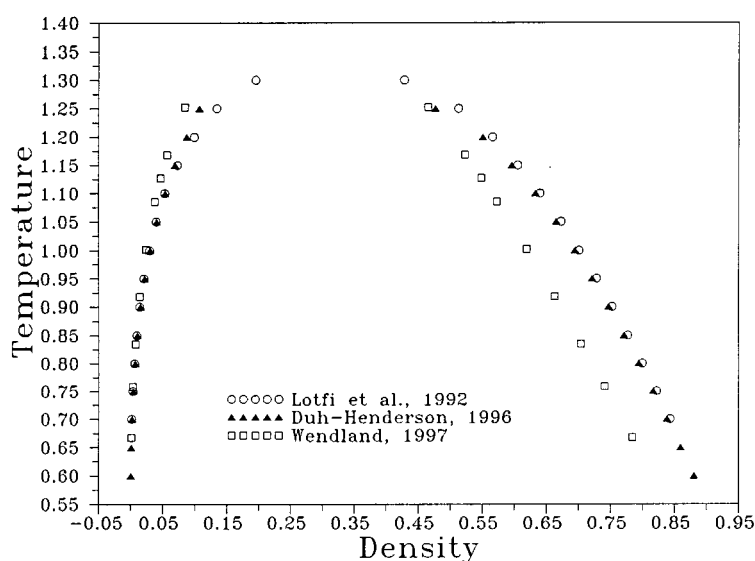


Fig. 1. VLE curves (densities versus temperature) for 3D LJ fluids obtained by Lotfi *et al.* (1992) and by using two theoretical equations (Duh and Henderson 1996; Wendland 1997).

Theoretical results for ρ_v and ρ_l have also been obtained recently from a new approach to the Born–Green–Yvon equation (Wendland 1997). These results are practically the same as those obtained from an EOS based on the attractive mean field approximation. However, as is shown in Fig. 1, there are major differences with respect to the Lotfi *et al.* (1992) results, and especially for the

liquid densities. The deviations are around 10% for ρ_v and around 20% for ρ_l . No data for either pressure or the chemical potential have been given.

Taking into account that the aforementioned theoretical results lead to results with high discrepancies with respect to those obtained in computer simulations, and that these theoretical methods do not give analytical expressions for the calculation of the thermodynamical properties, a more practical alternative seems to be the use of semi-empirical or semi-theoretical equations of state. For 3D LJ fluids, the VLE curves have been presented graphically by Johnson *et al.* (1993) and by Kolafa and Nezbeda (1994), for which they used their own EOSs. However, neither the method used nor the data are given in their publications. Their diagrams show that the vapour and liquid densities, as well as the vapour pressure, obtained from these EOSs are practically equal to those given by Lotfi *et al.* (1992), except for temperatures near the critical point. As Kolafa and Nezbeda (1994) use the Lotfi *et al.* (1992) data to fit the coefficients of their equation, and as is noted by the authors themselves, the KN EOS reproduces better the vapour density and pressure, especially for temperatures near the critical point. However, no numerical deviations are given by the authors.

In the present study, we solved equation (11) numerically, and then obtained the VLE coexistence properties (densities, pressure and chemical potential, in reduced LJ units) for the 3D LJ model from the JZG (2), KN (3), and our CM (5) EOSs in the range $T = 0.7$ – 1.3 (with intervals of 0.05 units). The results are listed in Tables 2 to 4. By comparing the values in these tables with those given by Lotfi *et al.* (1992), we found that the average of the absolute deviations (AAD) in the calculation of ρ_v is 3.0% for the JZG EOS, 1.7% for the KN, and 2.7% when our CM EOS is used. As can be seen in Fig. 2, the KN EOS gives results for the vapour density within the uncertainties of the Lotfi *et al.* (1992) results, except for $T = 0.85$, whereas the JZG and our CM EOSs systematically give values greater than the Lotfi *et al.* results.

For the liquid densities the corresponding AADs are 0.44%, 0.44% and 0.46%, respectively. However, the results for this ρ_l given by Lotfi *et al.* (1992) have only small uncertainties, so that these results are more difficult to reproduce when EOSs are used. As can be seen in Fig. 3, there are a good many results

Table 2. VLE properties for 3D LJ fluids obtained from the Johnson *et al.* (1993) EOS (2)

T	ρ_v	ρ_l	P	μ
0.70	0.00201	0.84324	0.00138	-3.67369
0.75	0.00366	0.82169	0.00266	-3.50516
0.80	0.00616	0.79887	0.00469	-3.34809
0.85	0.00974	0.77551	0.00772	-3.20258
0.90	0.01466	0.75166	0.01197	-3.06756
0.95	0.02121	0.72703	0.01777	-2.94182
1.00	0.02981	0.70117	0.02519	-2.82433
1.05	0.04096	0.67345	0.03469	-2.71424
1.10	0.05543	0.64299	0.04647	-2.61089
1.15	0.07449	0.60839	0.06083	-2.51376
1.20	0.10051	0.56692	0.07808	-2.42247
1.25	0.13941	0.51182	0.09859	-2.33677
1.30	0.21977	0.41019	0.12290	-2.25684

Table 3. VLE properties for 3D LJ fluids obtained from the Kolafa–Nezbeda (1994) EOS (3)

T	ρ_v	ρ_l	P	μ
0.70	0.00199	0.84277	0.00136	−3.68237
0.75	0.00361	0.82186	0.00262	−3.51487
0.80	0.00608	0.80012	0.00463	−3.35914
0.85	0.00960	0.77740	0.00767	−3.21428
0.90	0.01446	0.75352	0.01181	−3.07943
0.95	0.02095	0.72824	0.01748	−2.95380
1.00	0.02946	0.70127	0.02487	−2.83667
1.05	0.04049	0.67218	0.03425	−2.72738
1.10	0.05477	0.64033	0.04586	−2.62529
1.15	0.07335	0.60475	0.05995	−2.52982
1.20	0.09805	0.56375	0.07678	−2.44042
1.25	0.13241	0.51396	0.09662	−2.35658
1.30	0.18609	0.44593	0.11972	−2.27780

Table 4. VLE properties for 3D LJ fluids obtained from the CM EOS (5) (this work)

T	ρ_v	ρ_l	P	μ
0.70	0.00199	0.84404	0.00137	−3.67822
0.75	0.00368	0.82089	0.00267	−3.50118
0.80	0.00617	0.79879	0.00469	−3.34752
0.85	0.00971	0.77617	0.00769	−3.20515
0.90	0.01461	0.75226	0.01194	−3.06991
0.95	0.02121	0.72694	0.01770	−2.94179
1.00	0.02989	0.70036	0.02525	−2.82220
1.05	0.04107	0.67259	0.03477	−2.71205
1.10	0.05544	0.64305	0.04648	−2.61074
1.15	0.07428	0.60974	0.06069	−2.51588
1.20	0.10038	0.56819	0.07796	−2.42423
1.25	0.14007	0.50944	0.09883	−2.33490
1.30	0.21441	0.41379	0.12246	−2.25851

obtained with EOSs that lie outside these uncertainties. For $T = 1.3$, which is not shown in Fig. 3, only the CM expression gives a deviation less than the uncertainty of 3.5% given by Lotfi *et al.* (1992).

In the case of the vapour pressure, the AADs are 1.8%, 1.1% and 1.7% for the JZG, KN and CM EOSs, respectively. As can be seen in Fig. 4, the KN EOS gives values that are always within the uncertainties given by Lotfi *et al.* (1992). Here the maximum deviations are found at $T = 0.7$, i.e. at the temperature of the triple point.

From the above results, we can conclude that there is good agreement between the values for the VLE properties of 3D LJ fluids obtained from EOSs and those obtained from computer simulations. The maximum deviations are found near the critical point ($T = 1.3$) for the vapour and liquid densities, and near the triple point ($T = 0.7$) for the vapour pressure. The semi-theoretical EOSs, including the one proposed here, give results a little better than those obtained from semi-empirical EOSs. In particular, the KN EOS gives excellent results except for the liquid density at $T = 1.3$. Our CM EOS, which is only cubic

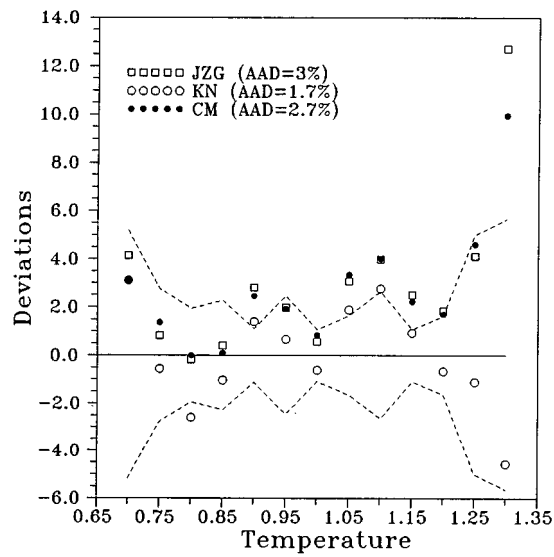


Fig. 2. Deviations between values for the vapour density of 3D LJ fluids obtained from EOSs (points) and those given by Lotfi *et al.* (1992), together with the uncertainties in the latter (curves).

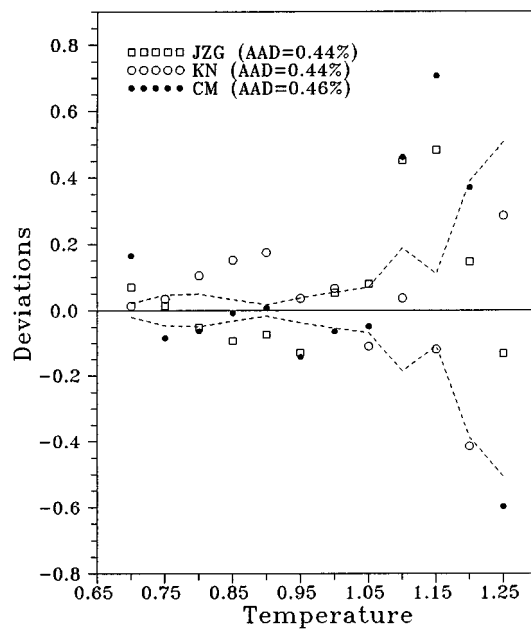


Fig. 3. Deviations between values for the liquid density of 3D LJ fluids obtained from EOSs (points) and those given by Lotfi *et al.* (1992), together with the uncertainties in the latter (curves).

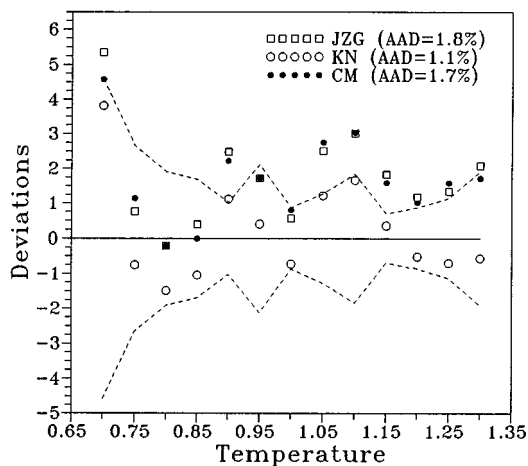


Fig. 4. Deviations between values for the vapour pressure of 3D LJ fluids obtained from EOSs (points) and those given by Lotfi *et al.* (1992), together with the uncertainties in the latter (curves).

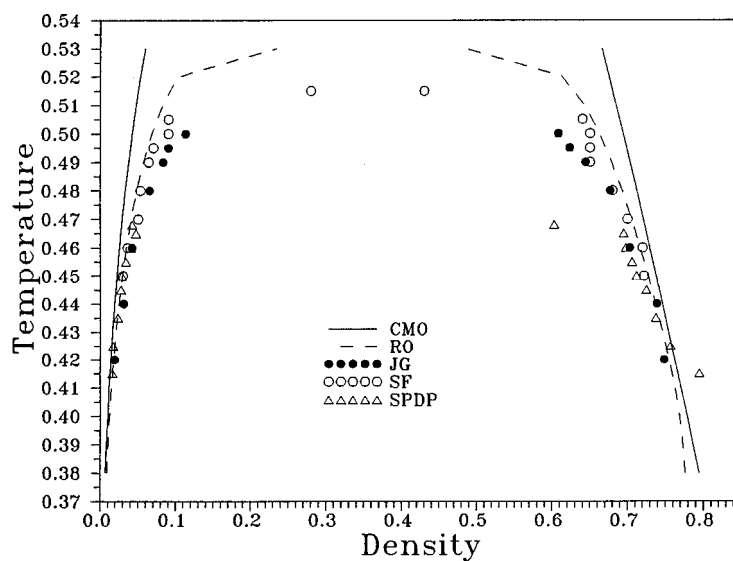


Fig. 5. VLE curves (densities versus temperature) for 2D LJ fluids obtained from computer simulations [points: SPDP, Singh *et al.* (1990); SF, Smit and Frenkel (1991); JG, Jiang and Gubbins (1995)], from the RO EOS (2), and from the CMO EOS (5).

in density, gives similar results to those obtained with the JZG EOS (which is analytically more complex and has no theoretical basis). In particular, excellent results are obtained with the CM expression for temperatures near 0.85 (see Figs 2–4) and in the case of the liquid density for $T = 1.3$.

If the uncertainties in the results given by Lotfi *et al.* (1992) are taken into account, then the KN EOS is the only one that gives adequate results (within these uncertainties) for the vapour density and pressure over the full temperature range. Although the liquid density is the property that is most accurately determined, the deviations obtained by using EOSs are greater than the uncertainties in the computer simulations.

(3b) Two-dimensional Lennard-Jones Fluids

We examine here three sets of data for the VLE properties of 2D LJ fluids obtained from computer simulations. First, we consider that given by Singh *et al.* (1990), in the range $T = 0.415\text{--}0.468$, with uncertainties between 2.9% and 6% (at $T = 0.468$) for ρ_v and between 0.4% and 10% (at $T = 0.468$) for ρ_l . No data for the pressure or the chemical potential were reported by the authors. Second, Smit and Frenkel (1991) gave results in the range $T = 0.45$ to 0.515 , with uncertainties of 7% to 40% and 1.2% to 6.2% for the vapour and liquid densities, respectively, and with maximum uncertainties of 31%, 300%, 9% and 28% in the determination of P_v , P_l , μ_v and μ_l , respectively. Third, we consider the most recent computer simulation of Jiang and Gubbins (1995), where uncertainties are not given and only ρ_v and ρ_l data are published. The VLE curves obtained in these three computer simulations are shown in Fig. 5.

Smit and Frenkel (1991) assert that their VLE curve is in good agreement with those presented by Singh *et al.* (1990). However, we can see in Fig. 5 that their results can be compared only for two temperatures ($T = 0.45$ and 0.46). We find that their ρ_v data are in agreement (within their uncertainties), whereas great differences are found in the case of the liquid densities.

When the Smit and Frenkel (1991) results are compared with those of Jiang and Gubbins (1995) (see Fig. 5), we find that the vapour densities coincide, within the great uncertainties of the former, only at $T = 0.46$. With respect to the liquid densities, where the uncertainties are lower, the results are in good agreement only in the range $T = 0.48\text{--}0.495$, with great deviations occurring at lower or higher temperatures.

Finally, the data given by Singh *et al.* (1990) can be compared with the Jiang and Gubbins (1995) data only for $T = 0.46$, where excellent agreement is found (see Fig. 5).

In general, all the results for ρ_v obtained in the aforementioned computer simulations can be considered as equal in the range $0.41 \leq T \leq 0.46$. For $T > 0.46$, and especially for T near to or greater than 0.5 , the results are very different. For the liquid density, the data given by Singh *et al.* (1990) must be taken as good only for $0.42 \leq T \leq 0.46$, whereas for $0.46 \leq T \leq 0.49$ the values given by Smit and Frenkel (1991) or by Jiang and Gubbins (1995) are adequate. No conclusions can be drawn for $T > 0.49$. Finally, for the vapour pressure, the lack of results in the case of the Jiang and Gubbins (1995) computer simulation and the great uncertainties reported by Smit and Frenkel (1991) do not permit these studies to be taken as a clear reference for comparison with theoretical results.

No calculations of VLE properties for 2D LJ fluids from EOSs have been reported until now. For instance, this calculation was not considered in the work of Reddy and O'Shea (1986). We therefore obtained these properties by solving

equation (11) and using the RO expression (2). Results are given in Table 5 and Fig. 5. As can be seen, the RO VLE curve is in good agreement with the computer simulation results of Smit and Frenkel (1991), while being only in minor agreement with the results of Jiang and Gubbins (1995) for $T > 0.45$.

Table 5. VLE properties for 2D LJ fluids obtained from the semi-empirical RO EOS (2)

T	ρ_v	ρ_l	P	μ
0.38	0.00854	0.77625	0.00297	-1.49547
0.39	0.01034	0.77350	0.00363	-1.47016
0.40	0.01244	0.76892	0.00442	-1.44455
0.41	0.01490	0.76276	0.00533	-1.41893
0.42	0.01776	0.75532	0.00639	-1.39352
0.43	0.02109	0.74685	0.00761	-1.36850
0.44	0.02494	0.73755	0.00899	-1.34397
0.45	0.02940	0.72752	0.01055	-1.32000
0.46	0.03460	0.71677	0.01232	-1.29661
0.47	0.04070	0.70521	0.01430	-1.27380
0.48	0.04794	0.69262	0.01652	-1.25156
0.49	0.05672	0.67859	0.01902	-1.22985
0.50	0.06772	0.66236	0.02181	-1.20865
0.51	0.08241	0.64220	0.02494	-1.18793
0.52	0.10504	0.61268	0.02853	-1.16768
0.53	0.23368	0.48612	0.03285	-1.14805

Table 6. VLE properties for 2D LJ fluids obtained from the CMO EOS (5)

T	ρ_v	ρ_l	P	μ
0.38	0.00681	0.79445	0.00250	-1.53955
0.39	0.00829	0.78669	0.00311	-1.50789
0.40	0.00997	0.77884	0.00381	-1.47734
0.41	0.01189	0.77088	0.00462	-1.44784
0.42	0.01405	0.76282	0.00555	-1.41935
0.43	0.01646	0.75464	0.00659	-1.39183
0.44	0.01915	0.74634	0.00777	-1.36523
0.45	0.02212	0.73793	0.00909	-1.33951
0.46	0.02541	0.72938	0.01055	-1.31464
0.47	0.02903	0.72069	0.01216	-1.29057
0.48	0.03299	0.71187	0.01393	-1.26728
0.49	0.03734	0.70290	0.01586	-1.24472
0.50	0.04209	0.69377	0.01796	-1.22287
0.51	0.04727	0.68447	0.02023	-1.20168
0.52	0.05293	0.67500	0.02268	-1.18113
0.53	0.05911	0.66532	0.02532	-1.16118

Results were also obtained by using our CMO EOS (Cuadros *et al.* 1997). As is shown in Table 6 and Fig. 5, this EOS seems to be valid for the calculation of VLE densities only for low temperatures ($T \leq 0.46$). By comparing the results in Tables 5 and 6, one sees there is a clear disagreement between the vapour pressures obtained from the RO and the CM equations, whereas a better agreement is found for the chemical potential values.

4. Conclusions

Vapour–liquid equilibrium properties for both 3D and 2D LJ fluids have been obtained from EOSs proposed by the authors in this (3D) and a previous work (2D). These semi-theoretical EOSs are based on the use of WCA theory expressions together with a fit to computer simulation results. Results were compared with those obtained from computer simulations or from other (more complex) semi-empirical or semi-theoretical equations of state.

For 3D LJ fluids we took the results obtained by Lotfi *et al.* (1992) as the best reference for comparison with theoretical results. We also considered the results reported recently by Duh and Henderson (1996), who use a new integral equation theory. We found major numerical discrepancies with respect to the results of Lotfi *et al.* (1992), except in the case of the liquid density. Also, the most recent results given by Wendland (1997) using a new approach to the Born–Green–Yvon equation are in great disagreement with their previous ones (Wendland 1997).

We also solved numerically the equations that give the coexistence properties (densities, pressures and chemical potentials) for the 3D LJ model by using the semi-empirical JZG EOS, the semi-theoretical KN EOS and a new cubic-in-density EOS proposed in the present work. Good agreement was found with the results obtained by Lotfi *et al.* (1992). The maximum deviations are found near the critical or the triple point. The liquid density is the property that is most accurately determined. However, the deviations obtained by using EOSs are greater than the uncertainties in the computer simulations. In particular, the KN EOS gives excellent results [within the uncertainties of the Lotfi *et al.* (1992) results] for the vapour density and vapour pressure. Our EOS, which is only cubic in density and thus simpler, gives similar results to those obtained with the others.

For 2D LJ fluids we compared and contrasted the results given in three different computer simulations. Values given for the vapour and liquid densities are similar only for low temperatures ($T \leq 0.46$), being very different near the critical point. No adequate data for the vapour pressure have been reported in these computer simulations so that no adequate comparison with theoretical results is possible.

We obtained the VLE properties for 2D LJ fluids from the semi-empirical RO EOS and a simple cubic-in-density EOS proposed by some of us in a previous work. The two EOSs give similar results for the coexistence densities at low temperatures, these results being in good agreement with those obtained through computer simulations. For high temperatures, i.e. for temperatures near the critical point, the RO EOS, which is analytically more complex, seems to present better behaviour. Results for the vapour pressure obtained from the RO and our EOS are in marked disagreement.

In conclusion, we would like to emphasise that the proposed models, being simpler and having a clearer separation of the contributions of the repulsive and attractive forces than other analytical expressions, allow us to determine the VLE properties of both 3D and 2D LJ fluids, giving results close to those obtained from computer simulation data.

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