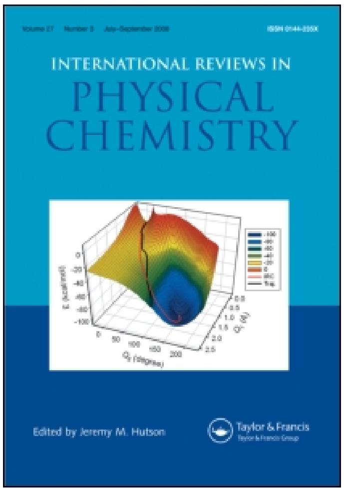

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Thermodynamics of simple fluids following the Weeks–Chandler–Andersen picture

By F. CUADROS†, A. MULERO
Departamento de Física, Universidad de Extremadura, 06071 Badajoz, Spain

W. OKRASINSKI
Institute of Mathematics, University of Wrocław, Wrocław, Poland

and W. AHUMADA
Departamento de Física, Universidad Católica del Norte, Antofagasta, Chile

In this work we propose some new analytic expressions that describe the thermodynamics of simple fluids. These equations have a strong theoretical background (they are based on the Weeks–Chandler–Andersen perturbative theory), combine accuracy with simplicity and are valid over a wide range of temperatures and densities. Predictions of the thermodynamics of the vapour–liquid equilibrium and molar heat capacity at a constant pressure for methane are made, giving good agreement with experimental results, and being compared with the predictions of the well known Soave equation.

1. Introduction

For chemical engineering applications it is necessary to dispose of simple and accurate mathematical models to predict the thermodynamic behaviour of pure fluids and their mixtures. We think that *A good thermodynamic model of simple fluids will be the basis for studying other more complex fluids and fluid mixtures*, and this is a general goal pursued by our research group, and we can say that it has been reached in a satisfactory way in the case of simple fluids. Indeed, our models (Cuadros and Ahumada 1996, Cuadros and Okrasinski 1996) have been analysed and contrasted with other equations of state (EOSs) published in the literature (Johnson *et al.* 1993, Kolafa and Nezbeda 1994). Our models have very simple expressions, whereas the above-mentioned EOSs have more than 30 parameters, some of them nonlinear; so their mathematical handling is very complicated. Despite their simplicity, our models predict very accurately the vapour–liquid equilibrium (VLE) as well as the molar heat capacity values at a constant pressure, for simple fluids.

Other advantages, with respect to other theoretical models, is that we can simultaneously require the coexistence of thermal, mechanical and chemical equilibria and can avoid lack of thermodynamic consistency of the above-mentioned EOSs. For example we have observed that for some states where these EOSs obtain equality between the liquid and vapour pressures for VLE calculations, the difference between the chemical potentials is greater than 100%.

Finally, another defect of these EOSs, which is common to other EOSs obtained from correlations of experimental data, is the absence of a theoretical background,

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† E-mail: cuadros1@ba.unex.es.

making the extrapolation to other temperature and density ranges from those deduced very difficult.

For the progressive elimination of these difficulties we have proposed simple analytic equations that predict the equilibrium properties of simple fluids with sufficient accuracy (Cuadros *et al.* 1993, Cuadros and Ahumada 1996, Cuadros and Okrasinski 1996, Cuadros *et al.* 1996b). The above-mentioned equations have been obtained from computer molecular dynamics (MD) and using the general expressions of the Weeks–Chandler–Andersen (WCA) (1971) theory.

This work has been organized as follows: section 2 is devoted to presenting the WCA theory, our proposed model and the Soave (1972) equation. In section 3 we compare computer simulation or theoretical results with experimental data. In section 4, we present the vapour pressure predictions obtained from our models together with the corresponding experimental values of methane, as well as with those obtained from the Soave EOS. In this section we analyse also the behaviour of our model in the calculation of the molar heat capacity at a constant pressure of liquid methane. In the last section we shall present a compilation of the most important conclusions and the possibility of extending our models to predict the thermodynamics of more complex fluids and liquid mixtures.

2. Thermodynamics of simple fluids

2.1. *The Weeks–Chandler–Andersen theory*

One of the most successful theories for simple fluids is the WCA (1971) theory. In previous years and on the basis of a great number of computer simulation results we have made an exhaustive and systematic study about its validity and range of applicability both in three and in two dimensions (Rull *et al.* 1984, Valderrama *et al.* 1990, Cuadros and Mulero 1992, Cuadros *et al.* 1996b). In fact, the WCA theory is very useful for solving very different problems (for example Matyushov and Schmid (1996) have used the WCA theory to study solvent effects).

The WCA theory is applicable to system with molecular interaction described by the Lennard-Jones (LJ) (1923) potential

$$u_{\mathrm{LJ}}(r) = 4\left[\left(\frac{1}{r}\right)^{12} - \left(\frac{1}{r}\right)^{6}\right] \tag{1}$$

and is based on the old van der Waals (vdW) idea of separating the contributions of the attractive and repulsive forces on the calculation of the thermodynamic properties (Cuadros *et al.* 1994). For the LJ potential the WCA separation is given by

$$U(r) = U_0(r) + \lambda U_{\mathrm{p}}(r), \tag{2}$$

where $U_0(r)$ is the repulsive part of the LJ potential with a strong slope (force) and short range, $U_{\mathrm{p}}(r)$ is the corresponding attractive part with a smooth slope (force) and long range that is treated as a perturbation and λ is a perturbative parameter that varies continuously from 0 to 1. When $\lambda = 0$, the intermolecular potential is purely repulsive (the system whose molecular interaction is given by $U_0(r)$ is called the reference system) while for $\lambda = 1$ we have the complete LJ potential. The λ variation from 0 to 1 permits us to follow the effect of the 'charge' of the attractive intermolecular forces on the thermodynamic properties of the system.

In previous and most of the following expressions all quantities are expressed in reduced LJ units. So the distances are divided by σ (the distance for which the LJ potential is equal to zero) and the energies are divided by ε (minimum depth well of the LJ potential). For simplicity, in this work we used an asterisk (*) to designate properties in 'real' units.

From equation (2) and following statistical mechanics arguments, we can obtain the expression for the excess of the Helmholtz energy per molecule respect to the ideal gas given by (Weeks and Broughton 1983)

$$A = A_0 - \rho\alpha(T, \rho), \tag{3}$$

where A_0 is the Helmholtz energy corresponding to the reference system, T is the temperature, ρ is the numerical density and $\alpha(T, \rho)$ is a function having the form

$$\alpha(T, \rho) = -2\pi \int_0^1 \left(\int_0^\infty U_{\mathrm{p}}(r)\, g_\lambda(r)\, r^2\, \mathrm{d}r \right) \mathrm{d}\lambda, \tag{4}$$

where $g_\lambda(r)$ is the radial distribution function (RDF) for a given value of λ. The physical meaning of the $\alpha(T, \rho)$ function, in the same way as the constant a in the vdW EOS, is to give the contribution of the intermolecular forces in the calculation of A, and therefore in the calculation of the thermodynamic properties.

If we differentiate A/T with respect to $1/T$, we obtain the potential energy per molecule:

$$E = E_0 - \rho\alpha(T, \rho) + \rho T \left(\frac{\partial \alpha(T, \rho)}{\partial T} \right)_{V,\, N}. \tag{5}$$

Differentiating equation (3) with respect to V, we obtain the pressure as follows:

$$P = P_0 - \rho^2 \alpha(T, \rho) - \rho^3 \left(\frac{\partial \alpha(T, \rho)}{\partial \rho} \right)_{T,\, N}. \tag{6}$$

Finally, using equations (3) and (6), the chemical potential μ can be obtained from

$$\mu = \mu_0 - 2\rho\alpha(T, \rho) - \rho^2 \left(\frac{\partial \alpha(T, \rho)}{\partial \rho} \right)_{T,\, N}. \tag{7}$$

For a given intermolecular potential separated as in equation (2), equations (3)–(7) are general and exact expressions.

In equations (5)–(7), E_0, P_0 and μ_0 are the corresponding quantities of the reference system ($\lambda = 0$). In previous work (Cuadros *et al.* 1993, 1996d) we have shown that the Carnahan–Starling (CS) (1969) (see also de Souza *et al.* (1994)) expressions are very appropriate for describing the thermodynamic quantities of the reference system if the hard-sphere diameter is given by the Verlet–Weis (1972) approximation

$$d(T) = \frac{0{\cdot}3837 + 1{\cdot}068/T}{0{\cdot}4293 + 1/T}. \tag{8}$$

Thus we shall use the following CS expressions for the reference system properties:

$$E_0 = -6T^2 \frac{1}{d} \left(\frac{\partial d}{\partial T} \right)_V \frac{2y - y^2}{(1 - y)^3}, \tag{9}$$

$$P_0 = \rho T \frac{1 + y + y^2 - y^3}{(1 - y)^3} \tag{10}$$

and

$$\mu_0 = T \frac{8y - 9y^2 + 3y^3}{(1 - y)^3} + T(\log \rho + 1), \tag{11}$$

where $y = \pi\rho d^3/6$.

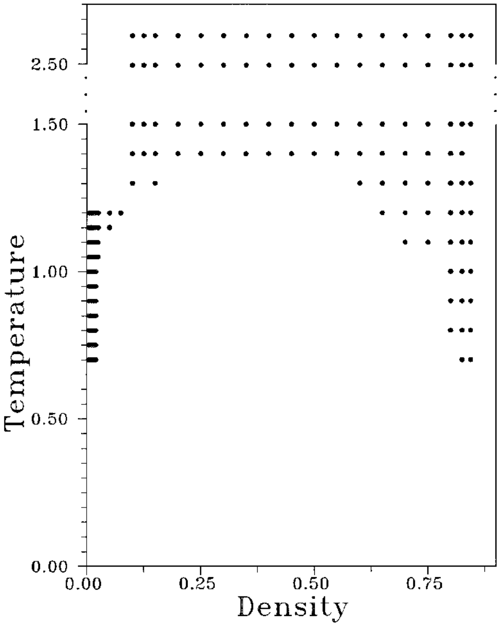

Figure 1. Simulated states. For the lowest densities we obtained results each 0•001 units of ρ (T = 0•7 to T = 1•20). For T from 1•5 to 2•6 we obtained results each 0•1 unit of temperature at the same densities shown for T = 1•0.

On the other hand, to obtain the thermodynamics properties following the WCA picture (equations (3)–(7)) it is necessary to calculate values of the $\alpha(T, \rho)$ function and its derivative with respect to the temperature and density. Our proposal is to use the well known computer stimulation technique to obtain the main structural and thermodynamics properties of the fluid (i.e. the RDF, P and E) for different values of the λ parameter (Cuadros and Mulero 1992, Cuadros *et al.* 1996b), as we shall describe in the next section.

2.2. *The proposed model*

In order to obtain an analytic expression of the thermodynamic properties of LJ fluids as functions of the thermodynamic state (T, ρ) we have performed an extensive MD computer simulation for LJ systems with the intermolecular potential separated as in equation (2). The simulated states have been around 700 corresponding to the supercritical, liquid and gaseous regions of the phase diagram (figure 1). The duration of each run was 5000 time steps following the procedure described in previous work (Rull *et al.* 1984, Cuadros *et al.* 1996b, Cuadros and Ahumada 1996). For each state (T, ρ) we obtained the pressure, potential energy per particle and RDF for five values of the λ parameters (λ = 0, 0•25, 0•5, 0•75 and 1•0). Using the RDF data, values of the $\alpha(T, \rho)$ function are obtained by integration of equation (4). A fitting of these results permits us to write an analytical expression which can be used to obtain E and P from equations (5) and (6), and finally to test these theoretical values with the computer simulation values.

In all cases the LJ potential was cut off at the reduced distance of 2•5; so the corresponding asymptotic contributions must be added.

On the other hand, we have shown (Cuadros and Ahumada 1996, Cuadros *et al.* 1996c, d) that it is necessary to carry out, at least, three fits if one wants to obtain a

Table 1. The coefficients for the fit of $\alpha(T,\rho)$ in the gaseous, liquid and supercritical regions, where $\alpha(T,\rho) = \alpha_1(T)+\alpha_2(T)\rho$, $\alpha_1(T) = b_1+b_2T+b_3T^2+b_4T^3$ and $\alpha_2(T) = b_5+b_6T+b_7T^2+b_8T^3$.

	Gaseous phase	Liquid phase	Supercritical phase
b_1	10·210	8·774	5·709
b_2	− 15·848	− 4·675	0·360
b_3	16·040	2·388	− 0·158
b_4	− 5·151	− 0·391	0·025
b_5	43·137	− 1·725	2·347
b_6	123·290	5·352	− 0·178
b_7	− 255·291	− 2·795	− 0·017
b_8	104·847	0·458	0·004

good mathematical description on the complete phase plane. So different fits of $\alpha(T,\rho)$ were made on the liquid, gas and supercritical regions, with the percentage mean deviations of 0·2%, 0·9% and 0·3%, respectively. The final analytical form and coefficients of the fits are shown in table 1. The three fitted $\alpha(T,\rho)$ functions are introduced into equations (5)–(7), and using equations (8)–(11) we are able to obtain the thermodynamics of our system in the three above-mentioned phase regions. In particular, the EOS for each region can be written as follows:

$$P(T,\rho) = P_0(T,\rho)-\alpha_1(T)\rho^2-2\alpha_2(T)\rho^3-1{\cdot}060\,94\rho^2, \qquad (12)$$

whereas the chemical potential has the form

$$\mu(T,\rho) = \mu_0(T,\rho)-2\alpha_1(T)\rho-3\alpha_2(T)\rho^2-1{\cdot}6048\,\rho, \qquad (13)$$

where the last terms of both equations are the asymptotic contributions.

The calculation of the molar heat, capacity C_p in reduced units, is made on the basis (Callen 1981)

$$C_p-C_v = \frac{Tv\tilde{\alpha}^2}{\chi_T}, \qquad (14)$$

where $C_v = \frac{3}{2}+(\partial E/\partial T)_v$ is the molar heat capacity at constant volume, $\tilde{\alpha} = (1/v)(\partial v/\partial T)_p$ is the thermal expansion coefficient, $\chi_T = -(1/v)(\partial v/\partial P)_T$ is the isothermal compressibility and v is the molar volume.

Since C_v can be obtained directly from equation (5), and the $\tilde{\alpha}$ and χ_T coefficients are obtained from the EOS (equation (12)), then using equation (14) the final analytic expression proposed for C_p is

$$C_p(T,\rho) = \frac{5}{2}+\left(\frac{\partial E_0}{\partial T}\right)_\rho+\rho T[\alpha_1''(T)+\rho\alpha_2''(T)]+\frac{Tv\tilde{\alpha}^2}{\chi_T}, \qquad (15)$$

where $\alpha_1''(T)$ and $\alpha_2''(T)$ are the second derivatives of $\alpha_1(T)$ and $\alpha_2(T)$ functions with respect to the temperature (see table 1).

2.3. *The Soave equation of state*

In order to compare our model with well known empirical or semiempirical equations commonly used in chemical engineering, we consider the Soave (1972) modification of the Redlich–Kwong equation. The Soave EOS has the form (in real units)

$$P^* = \frac{RT^*}{v^*-b}-\frac{a_c[1+m(1-T_r^{1/2})]^2}{v^*(v^*+b)}, \qquad (16)$$

where R is the ideal gas constant, $a_c = 0{\cdot}427\,47\,(R^2 T_c^{*2}/P_c^*)$, $T_r = T/T_c^*$ is the reduced temperature with respect to the critical temperature T_c^*, P_c^* is the critical pressure, b is the covolume, v^* is the molar volume and m is a parameter that has been related by Soave (1972) to the acentric factor ω through the expression

$$m = 0{\cdot}480 + 1{\cdot}574\,\omega - 0{\cdot}176\,\omega^2. \tag{17}$$

As we can observe, the Soave EOS is a cubic vdW-type EOS with two characteristic terms: the repulsive pressure $RT^*/(v^* - b)$ equals to the vdW repulsive pressure, and the attractive pressure

$$P_{\mathrm{at}} = \frac{a_c[1 + m(1 - T_r^{1/2})]^2}{v^*(v^* + b)}. \tag{18}$$

We state that the WCA theory as well as the Soave EOS are different generalizations of the vdW theory.

Table 2. Values of LJ parameters for Ar, Kr, CH_4 and N_2 from the second virial coefficient (a) and from the viscosity (b) taken from literature and percentage deviations relative to the minimum between the maximum and the minimum values of these parameters (equation (19)).

System	σ (Å)	ε/k (K)	$D(\sigma)$ (%)	$D(\varepsilon/k)$ (%)
Ar	3·504	117·7 (a)	6·17	51·34
	3·336	141·2 (a)		
	3·400	122·0 (a)		
	3·405	119·8 (a)		
	3·465	116·0 (b)		
	3·418	124·0 (b)		
	3·542	93·0 (b)		
Kr	3·827	164·0 (a)	7·05	21·14
	3·575	191·4 (a)		
	3·597	158·0 (a)		
	3·600	171·0 (a)		
	3·610	190·0 (b)		
	3·655	178·9 (b)		
CH_4	4·010	142·8 (a)	8·20	16·57
	3·783	148·9 (a)		
	3·706	159·7 (a)		
	3·817	148·2 (a)		
	3·822	137·0 (b)		
	3·797	144·0 (b)		
	3·758	148·6 (b)		
N_2	3·698	95·0 (a)	11·51	60·53
	3·710	95·9 (a)		
	3·745	95·2 (a)		
	3·613	103·0 (a)		
	3·362	128·1 (a)		
	3·681	91·5 (b)		
	3·749	79·8 (b)		

3. Comparison with experimental results

A comparison between theoretical or computer simulation data and values obtained from empirical equations or directly from experiments is never an easy task. As is well known, the behaviour of real systems cannot be fully described through theoretical considerations. Then a theoretical model must be seen as a first approximation for further improvements which will include deviations from the ideal.

If we consider the LJ interaction as a valid representation of the real intermolecular potential, we limit our comparison to classical simple fluids with approximately spherical molecules. For example, methane (CH_4) can be considered as a classical simple fluid (Croxton 1975) whose molecules are almost spherical.

Once this model is accepted, one has another difficulty; the comparison depends strongly on the LJ parameter σ and ε and there are many LJ parameters cited in the literature with very different values for the same fluid (Cuadros *et al.* 1993, 1995, 1996a). For example, table 2 lists LJ values for Ar, Kr, CH_4 and N_2 obtained from measurements of the second virial coefficient and viscosity. One can see that there is a deal of divergence among the values. Moreover, in table 2, we have extracted the maximum and minimum values of the LJ parameters for the systems considered above, as given by the different workers, and their relative percentage deviation defined as

$$D(x) = \frac{X_{\max} - X_{\min}}{X_{\min}} \times 100. \tag{19}$$

Thus the connection between theoretical or computer simulation results and experimental data depends on the choice of the LJ parameters. What are the appropriate values of the LJ parameters? What is the best pair? It may be that one of two theories is more exact than the second, but both are accepted and considered as useful because of the ability of the investigator to choose the appropriate values of LJ parameters inside this wide range of variation, as shown in table 2.

Recently we have solved this problem and we have proposed a new procedure to determine LJ parameters by forcing agreement between the values of the pressure obtained from empirical EOS in the low-density region of phase space (Cuadros *et al.* 1995, 1996a).

Normally, computer simulation results for thermodynamic properties are expressed in reduced units using the molecular version of the principle of corresponding states (PCS), that is using the parameters of the intermolecular potential. According to the PCS, the reduced values of thermodynamic properties are equal for substances modelled by the same potential function. To compare computer and/or theoretical results with experiment, it is necessary to convert from PCS reduced units to physical units. For the thermodynamic variables involved in an EOS (pressure P, density ρ and temperature T) their expressions in reduced LJ units are

$$\begin{aligned} P &= P^* \frac{\sigma^3}{\varepsilon}, \\ \rho &= \rho^* \sigma^3 = \frac{N}{v}\sigma^3, \\ T &= \frac{T^*}{\varepsilon/k}, \end{aligned} \tag{20}$$

where N is the number of molecules and k is the Boltzmann constant. To convert these reduced properties to the units normally used in an EOS, we must use the following expressions:

$$P^* = P\frac{(\varepsilon/k)\,R}{N_{\mathrm{A}}\,\sigma^3}\,\mathrm{atm},$$

$$v^* = \frac{1}{\rho^*} = \frac{N_{\mathrm{A}}\,\sigma^3}{\rho}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}, \qquad (21)$$

$$T^* = T\frac{\varepsilon}{k}\,\mathrm{K},$$

where $R = 82{\cdot}06$ atm cm^3 mol^{-1} K^{-1}, ε/k is in kelvins, σ is in centimetres and N_{A} is the Avogadro number ($6{\cdot}023 \times 10^{23}$ mol^{-1}). From equations (21), it is easy to see that the different pairs of LJ parameters give different values for the EOS properties. So before proposing new models to determine the thermodynamic properties of real substances, we must be sure that we have good values of the LJ parameters of real system, such as those proposed by ourselves (Cuadros *et al*. 1995, 1996a).

As we have mentioned above, the test of validity of our proposed model will be made through the comparison with experimental results and those obtained from Soave EOS, for methane.

The interaction parameters for methane used in the present work are $\sigma = 4{\cdot}015 \pm 0{\cdot}039$ Å and $\varepsilon/k = 140{\cdot}42 \pm 1{\cdot}11$ K (Cuadros *et al*. 1995, 1996a).

The experimental methane data are taken from the *Design Institute for Physical Property Data* (1993). In this reference, the following empirical correlation for the vapour pressure is proposed:

$$\ln P^*_{\mathrm{V}} = e_1 + \frac{e_2}{T^*} + e_3 \ln T^* + e_4\,T^{*2}, \qquad (22)$$

for temperatures from $T^*_{\text{triple}} = 90{\cdot}67$ K to $T^*_{\mathrm{C}} = 190{\cdot}58$ K; the pressure is given in pascals and the constants are $e_1 = 38{\cdot}664$ Pa, $e_2 = -1314{\cdot}7$ Pa K, $e_3 = -3{\cdot}3373$ Pa K^{-1} and $e_4 = 3{\cdot}0155 \times 10^{-5}$ Pa K^{-2}.

The molar capacity at constant pressure has the empirical correlation (*Design Institute for Physical Property Data* 1993),

$$C_p = \sum_{i=0}^{4} c_i T^i, \qquad (23)$$

where C_p is given in joules per kilomole per kelvin, and $c_0 = 3{\cdot}7042 \times 10^5$, $c_1 = -1{\cdot}1296 \times 10^4$, $c_2 = 148{\cdot}3$, $c_3 = -0{\cdot}8554$ and $c_4 = 1{\cdot}8563 \times 10^{-3}$ are the constant values for C_p. The units for $c_i (i = 0, \ldots, 4)$ are in joules (kelvins)$^{-(i+1)}$ per kilomole.

4. Results

Table 3 and figure 2 present the experimental vapour pressure (equation (23)) values for methane and the corresponding curves, respectively, obtained from our models (equations (12) and (13)) and from the Soave EOS (equation (16)), for temperatures from 107·3 to 178·9 K.

Table 3. Values of the experimental vapour pressure P_{exp} for methane, the vapour pressure P_{calc} calculated from our EOS (equation (12)) and the vapour pressure P_{Soave} obtained from the Soave EOS (equation (16)).

T (K)	P_{exp} (atm)	P_{calc} (atm)	P_{Soave} (atm)
107·3	0·72	0·97	
108·8	0·82	1·08	
110·2	0·92	1·20	
111·6	1·04	1·32	
113·1	1·17	1·47	
114·5	1·31	1·64	
116·0	1·46	1·79	
117·3	1·63	2·02	
118·8	1·81	2·23	
120·2	2·00	2·49	
121·6	2·21	2·64	
123·1	2·44	2·87	
124·5	2·68	3·16	
125·9	2·94	3·43	
127·4	3·22	3·66	
128·8	3·52	3·99	
130·2	3·84	4·34	
131·7	4·18	4·60	
133·1	4·54	4·95	
134·5	4·92	5·39	
136·0	5·33	5·77	
137·4	5·76	6·18	
138·8	6·21	6·68	
140·2	6·69	7·12	
141·7	7·20	7·59	
143·1	7·73	8·09	
144·5	8·30	8·61	
146·0	8·89	9·20	
147·4	9·51	9·76	
148·8	10·16	10·34	
150·3	10·84	11·02	
151·7	11·56	11·63	
153·1	12·31	12·28	
154·6	13·09	13·07	
156·0	13·91	13·80	
157·4	14·77	14·50	
158·8	15·66	15·32	
160·3	16·59	16·12	
161·7	17·56	16·79	
163·1	18·57	17·61	
164·6	19·62	18·34	
166·0	20·71	19·16	
167·4	21·85	20·01	
168·9	23·03	20·95	
170·3	24·26	22·03	25·87
171·7	25·53	23·18	27·00
173·2	26·85	24·35	28·21
174·6	28·22	25·58	29·45
176·0	29·64	26·75	30·64
177·4	31·11	28·04	31·95
178·9	32·64	29·39	33·42

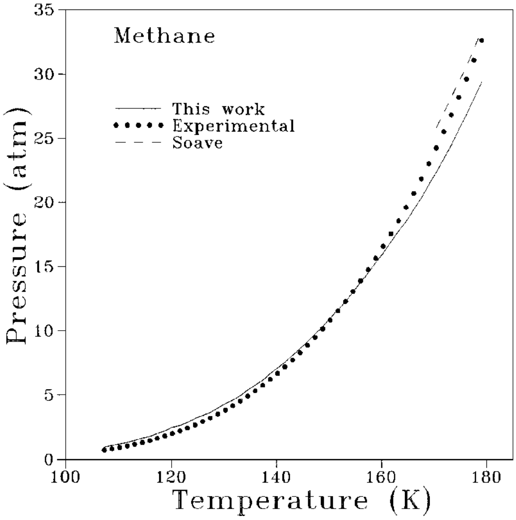

Figure 2. The experimental vapour pressure for methane, the vapour pressure calculated from our EOS (equation (12)) and the vapour pressure obtained from the Soave EOS (equation (16)).

As is shown, we obtain good agreement between our theoretical predictions and the experimental results for the above-mentioned system. In particular, the deviations are less than 10% on the temperature range 131–178 K. For temperatures below 131 K the deviations are greater.

The vapour pressure predictions for the methane obtained from the Soave EOS are calculated using the method of equality of the areas for each temperature. This is equivalent to the equality of the chemical potentials corresponding to the gaseous and liquid phases, at a given temperature. Nevertheless, we would like to point out that (Cuadros *et al.* 1996c, d), in practice, the accurate determination of the position of the rectilinear line of the isotherm for which pressures and areas must be equal is not a trivial problem. Figure 3 shows the Soave isotherm for methane near the critical point. As we can see, the isotherm has a strong slope for molar volumes corresponding to the liquid phase. So a small deviation in the determination of the rectilinear line, that is a small deviation in the quality between areas (equality of chemical potentials), involves a small deviation in the molar volume v_l corresponding to the liquid phase and the molar volume v_g corresponding to the gaseous phase. Because of the strong slope of the pressure in the liquid region, the difference in the determination of v_l is extraordinarily amplified when we determine the liquid pressure P_l, and hence so is the difference in the determination of the mechanical equilibrium between both phases.

We think that this procedure is not good and that the determination of VLE must be made on the basis of simultaneous equality of the pressures and chemical potentials between both phases, at a given temperature, using analytic expressions of the pressure and chemical potential as functions of the thermodynamic state (T, ρ), with the exception of the neighbourhood of the critical state, as we propose in the present work.

Moreover, from the Soave EOS, we have obtained reasonable results for temperatures greater than 170 K (see table 3 and figure 2). Below this temperature we obtain negative pressures and hence it is not possible to use the equality of the areas method to determine the VLE curves.

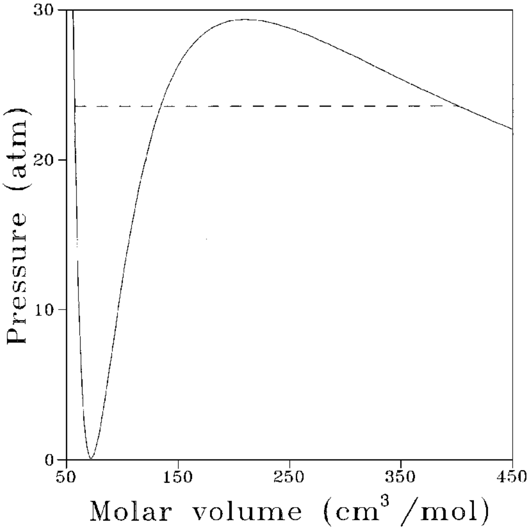

Figure 3. An isotherm close to the critical point of the methane obtained from the Soave EOS (equation (16)).

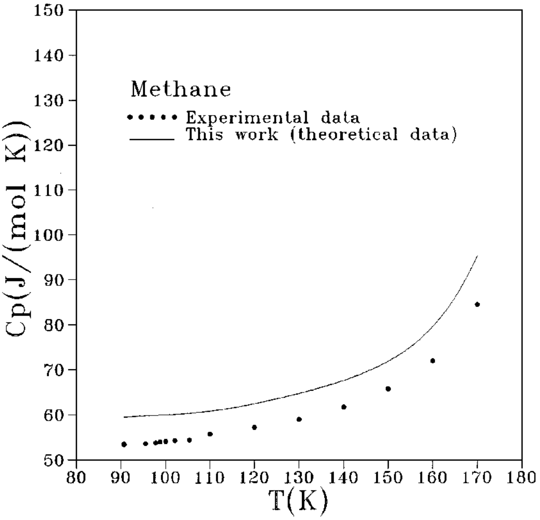

Figure 4. The theoretical molar heat capacity from equation (15) and the experimental value for methane at a pressure of 30 atm.

To complete our analysis, we compare the theoretical curve for the molar heat capacity at constant pressure, obtained from equation (15) and the corresponding experimental data for the methane (equation (23)) (*Design Institute for Physical Property Data* 1993) for a constant pressure equal to 30 atm. (For methane the critical pressure is $P_c^* = 45{\cdot}43$ atm, and the triple point pressure is $P_t^* = 0{\cdot}1157$ atm.) As we can see in figure 4, we again obtain excellent agreement (deviation less than 10%) between our theoretical results and the experimental data in all the total range of temperatures considered.

Now, we would like to attract attention about the analytic expression of C_p (equation (15)). Firstly, the C_p equation is related to the derivative C_v of the internal energy with respect to T, and to the derivatives $\tilde{\alpha}$ of the molar volume with respect to

T, and to the derivative χ_T of the molar volume with respect to P. As both $\tilde{\alpha}$ and χ_T are obtained from EOS (equation (12)), then the agreement between the theoretical and experimental values of C_p indicates that these are very good mathematical models (not only globally but locally) for calculating the Helmholtz energy, and hence to obtaining its first derivatives as internal energy and the EOS. Secondly, it is necessary to emphasize that C_p, $\tilde{\alpha}$ and χ_T are obtained through the first derivatives of the internal energy and EOS, that is from second derivatives of the Helmoltz energy. So one must have not only good global fits of the thermodynamic properties but (and this is very important) good local fits of these quantities in each thermodynamic state, as in our proposed model.

5. Conclusions

(1) We have proposed new and accurate mathematical models to calculate the thermodynamic properties of the simple fluids in the three phase regions: gaseous, liquid and supercritical.
(2) The analysis of our predictions about the thermodynamics of VLE shows that they are very good (errors less than 10% for the vapour pressures of the methane) in a wide range of temperatures.
(3) Empirical EOSs, such as the Soave EOS, give negative pressures for simple systems (methane, noble gases, nitrogen, etc.) and for temperatures very near to and below the critical temperature. This makes the empirical EOSs invalid for calculations.
(4) We have justified the need for obtaining the VLE curve on the basis of satisfying simultaneously the thermodynamic requirements of thermal, mechanical and chemical equilibria, using good and precise mathematical models as a function of the thermodynamic state (T, ρ).
(5) To complete this study we have analysed the behaviour of our models when they are compared with experimental data of the molar heat capacity at a constant pressure of the methane, finding again excellent agreement on a wide range of temperatures.
(6) This good agreement between theoretical and experimental C_p values requires that the expressions to calculate the internal energy and the EOS must be very accurate, not only globally but also locally.
(7) Despite their mathematical simplicity, our models are confirmed as very good to describe the thermodynamics of simple fluids. Moreover their theoretical background (they are based on the WCA theory) will permit us in the near future to adapt them to study thermodynamically other more complicated substances (polyatomic molecules), polar fluids and fluid mixtures inside a wide and ambitious research programme that we think will be very useful to chemical engineering.

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