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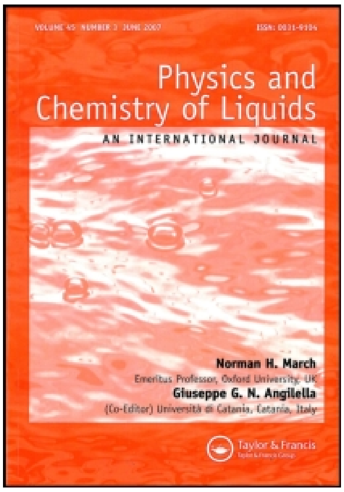

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Improving the prediction of liquid saturation densities from models based on the corresponding states principle

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Improving the prediction of liquid saturation densities from models based on the corresponding states principle

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The liquid saturation density of pure fluids is commonly predicted using models based on the corresponding states principle. Nevertheless, it is well-known that these models are not always accurate near the triple point. In this work we use simple modifications of several of those models in order obtain good accuracy at any temperature. In particular, for each model we change a fixed coefficient to a variable coefficient, which permits the model to reproduce exactly the value of the density at the triple point. The accuracy of a model based on a scale-variable-reduced-coordinate framework, and of a new simple predictive model recently proposed by us is also checked. This latter model does not contain adjustable coefficients but only two variable coefficients that depend on the temperature and density at both the critical and the triple point. We find that a simple modification of the well-known and straightforward Rackett model gives excellent accuracy (mean average absolute deviation 0.9%) in the whole temperature range for 107 fluids of different kinds.

Keywords: Vapor–liquid equilibrium; Liquid saturation density; Pure fluids; Corresponding states principle

1. Introduction

The calculation of saturated densities of pure substances at vapor–liquid equilibrium is essential for important practical applications, and serves as the basis for calculating other properties such as the surface tension [1–6].

There are many accurate empirical correlations giving the saturation liquid density. The simplest are based on applying the corresponding states principle (CSP) with the critical density and temperature, and the acentric factor as input data [1,4,7–11]. There are also proposals that include at least one [11–14] or more [15–17] adjustable parameters or a modified property such as the critical density [18].

The accuracy and applicability of these models to different kinds of fluids, generally in the temperature range where experimental data are available, have been extensively

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studied and some recommendations for the use of one or another method have been made [1,4,19–24]. Obviously, correlations that include adjustable parameters are more accurate than those without them. Nevertheless, their disadvantage is the need for experimental data against which to evaluate these adjustable parameters, with the concomitant relative lack of predictability. In any case, it is very important to choose the appropriate model for a given kind of fluid or even for a particular fluid at a particular temperature [25], i.e., there is no universal model that yields very accurate results for all kinds of fluids. As is well-known [10,23,24], the models based on the corresponding states principle do not always give accurate results far from the critical point, in particular, near the triple point.

Shaver *et al.* [26] proposed a scaled-variable-reduced-coordinate framework for correlating liquid saturation densities. They used the triple point temperature and saturation density as references to define new variables that are related by a new analytical expression. The correlation framework is essentially empirical, but permits to reproduce the saturation liquid densities of 22 fluids of different kinds with a mean absolute average percentage deviation (AAD) of only 0.1% when three adjustable coefficients are used. When not adjustable coefficients are used, the acentric factor and the critical compressibility factor are needed as additional inputs. This predictive version of the model, which we shall call SRG, includes 10 fixed coefficients, obtained by a fitting procedure, and it gives a mean AAD of 0.82% for the 34 fluids studied [26].

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Recently, we have proposed a new, simple, and predictive model for calculating both the vapor and the liquid saturation densities of pure fluids [27]. It is based on the symmetry of the derivatives of the two saturation densities with respect to the temperature, which is a consequence of applying the rectilinear diameter law. It does not contain adjustable coefficients, and only two coefficients have to be calculated for each fluid using straightforward analytical expressions. The required inputs are the critical temperature and density and also the triple point temperature and density. The findings were presented in reference [27], where only qualitative, but no numerical results were given. Results for different kinds of fluids were compared with those obtained with the most recent and accurate CSP model that predicts the saturation liquid density – the SNM0 model proposed by Mchaweh *et al.* [11] and with data taken from the NIST database. We found that the model is adequate even for those fluids for which SNM0 is less accurate. Moreover, the adequacy of the results does not depend on which fluid is being studied (unlike the case with the other simple models) as long as the rectilinear diameter law holds (which is not the case for water, for example). The qualitative results given in ref. [27] also include the vapor density, which can be obtained from the rectilinear diameter law.

The foregoing results led us to study the accuracy of simple modifications of the CSP models by changing one of the fixed coefficients of the model to a variable coefficient which depends on the temperature and density at both the critical and the triple points for each fluid. Thus, the models are forced to be accurate near both the triple and the critical point temperatures. The accuracy at other temperatures depends on the model used.

In this work we check the accuracy of the predictions of the liquid saturation density, for the whole vapor–liquid temperature range, of these modified models, as well as of the SRG model [26] and a model recently proposed by us [27]. In particular, we modified the Rackett [7], the so-called RRPS [1], and the SNM0 [11] models. The predictions are compared with data accepted in the DIPPR database [28] for

107 fluids of different kinds. The results for some particular families of fluids are also studied.

2. Models

As is well-known, the simplest expression giving the liquid saturation density, ρ, of fluids is that proposed by Rackett [7]:

$$\rho = \left[V_C a^{(1-T_r)^{2/7}} \right]^{-1}, \tag{1}$$

where V_C is the critical volume, $T_r = T/T_C$ is a reduced temperature, and T_C is the critical temperature. Originally Rackett [7] used the critical compressibility factor, Z_C, for the a coefficient. Subsequently, Yamada and Gunn [8] changed the value of $a = Z_C$ in equation (1) to a linear expression on the acentric factor, ω, which includes two fixed coefficients. Poling *et al.* [4] have shown that this modification leads to a clear improvement over the Rackett model.

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Our proposal here is to define the coefficient a by fixing the value of the density at a given temperature. In particular, if we take that temperature as the one at the triple point (T_T, ρ_T) then

$$a = \left(\frac{\rho_C}{\rho_T} \right) (1 - T_T/T_C)^{-2/7}. \tag{2}$$

Thus, the new coefficient a is different for each substance, as was the case in both the Rackett and the Yamada and Gunn models, but its use must improve the prediction of the density for the whole vapor–liquid equilibrium temperature range when compared with the original model. We shall call this the m-Rackett model.

Obviously, the degree of improvement may be different for each fluid because the behaviour is different at intermediate temperatures. Of course, there is no great improvement for those fluids for which the Rackett and/or the Yamada and Gunn models give good results at the triple point. Examples of fluids with this behaviour are as different as methane, 2-methylhexanoic acid, and hexafluoroethane (figure 1). For most fluids, however, the Rackett equation underestimates (figure 2a) or overestimates (figure 2b) the saturation liquid density at low temperatures, and then we find a great degree of improvement when the m-Rackett model is used. In any case, the model is not completely universal or perfect. Thus, for some fluids the use of the m-Rackett model gives a significantly lower deviation with respect to the experimental data, but it does not reproduce them exactly. Examples are hydrogen chloride, tetrachloroethylene, *trans*-3,5-dimethoxystilbene, and indole (figure 3). Finally, there are a few fluids (e.g., nitrogen dioxide, nitric oxide, and water) for which the Rackett model gives better results than the m-Rackett one at high temperatures, but the contrary is the case at low temperatures. An extreme example is ethanol (figure 4).

We note that the exponent (2/7) in equation (1) can be also replaced by a function of both the critical and triple temperatures and densities (instead of modifying the coefficient a), but that function also includes the critical compressibility factor as input. Moreover, as is shown in the examples of figure 5, the curvature of the function

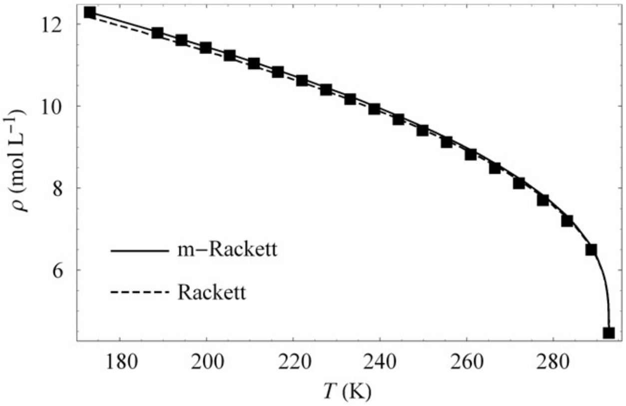

Figure 1. Saturated liquid density *vs*. temperature for hexafluoroethane. Lines: Rackett and m-Rackett predictions; points: DIPPR accepted data [28].

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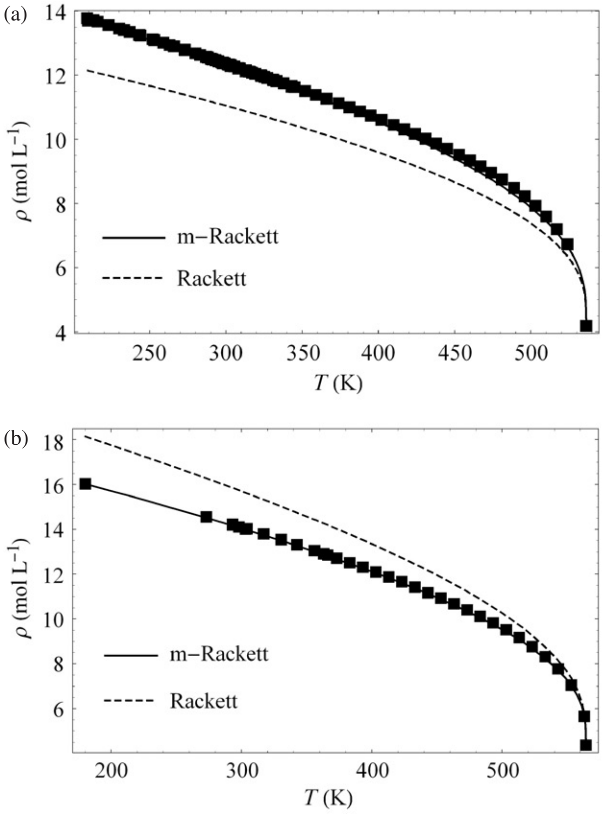

Figure 2. Saturated liquid density *vs*. temperature for (a) chloroform and (b) propionitrile. Lines: Rackett and m-Rackett predictions; points: DIPPR accepted data [28].

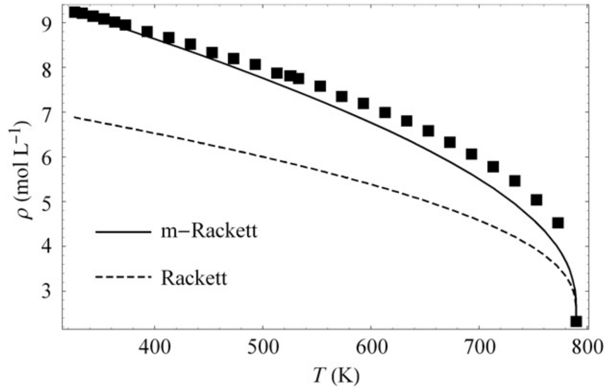

Figure 3. Saturated liquid density *vs*. temperature for indole. Lines: Rackett and m-Rackett predictions; points: DIPPR accepted data [28].

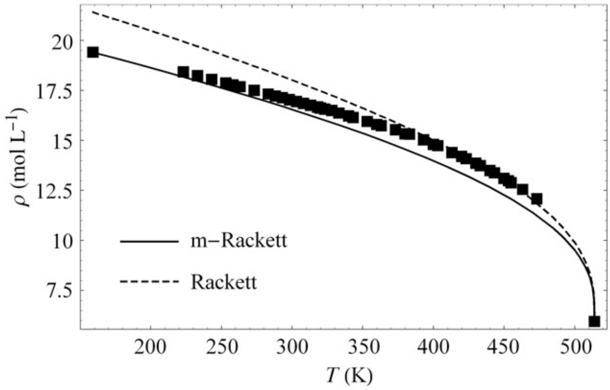

Figure 4. Saturated liquid density *vs*. temperature for ethanol. Lines: Rackett and m-Rackett predictions; points: DIPPR accepted data [28].

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obtained is not adequate for most fluids, especially for some fluids, such as indole and sodium chloride, for which the model diverges at the critical point.

Another correlation is that proposed by Reid *et al*. [1], which we shall call the RRPS correlation. It is based on a proposal of Riedel [29], and does not include the temperature in the exponent:

$$\rho = \rho_C\big(1 + b_1(1 - T_r) + b_2(1 - T_r)^{1/3}\big), \tag{3}$$

with

$$b_1 = 0.85 \quad \text{and} \quad b_2 = 1.6916 + 0.984\omega. \tag{4}$$

Nasrifar and Moshfeghian [14], in a test of the accuracy of equation (3) for 15 pure refrigerants over a wide temperature range, find an average deviation of 1.1%. The accuracy of the RRPS model in reproducing the liquid saturation density of 30 families of fluids has been studied in a previous work [23,24].

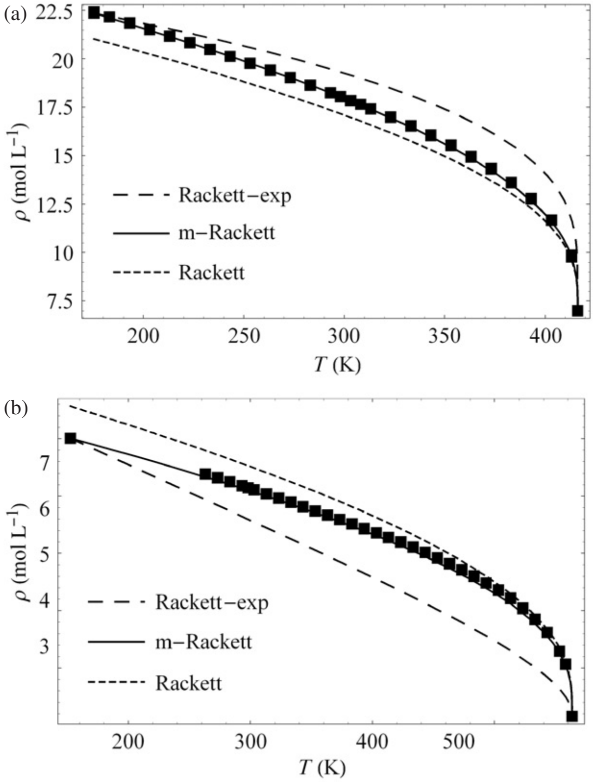

Figure 5. Saturated liquid density *vs.* temperature for (a) methyl chloride and (b) 3-methylheptane. Lines: Predictions from Rackett and m-Rackett models, and from the model obtained by replacing the exponent (2/7) in equation (1) by a substance-dependent coefficient (Rackett-exp).

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In order to improve the accuracy of the RRPS near the triple point, two modifications are possible:

- The first, which we called RRPS1 model, is to maintain the expression for b_2 and define a new b_1:

$$b_1 = \frac{(\rho_T/\rho_C) - 1 - b_2(1 - T_T/T_C)^{1/3}}{1 - T_T/T_C} \quad \text{and} \quad b_2 = 1.6916 + 0.984\omega. \tag{5}$$

  In this case, both the b_1 and b_2 coefficients are different for each substance and depend on the acentric factor.

- Our second proposal is to maintain the value of b_1 and then to define a new b_2 coefficient as

$$b_1 = 0.85 \quad \text{and} \quad b_2 = \frac{(\rho_T/\rho_C) - 1 - b_1(1 - T_T/T_C)}{(1 - T_T/T_C)^{1/3}}. \tag{6}$$

  This model, which we call RRPS2, has therefore a fixed coefficient and a variable coefficient, and, when compared with RRPS1, it needs one input parameter less (the acentric factor).

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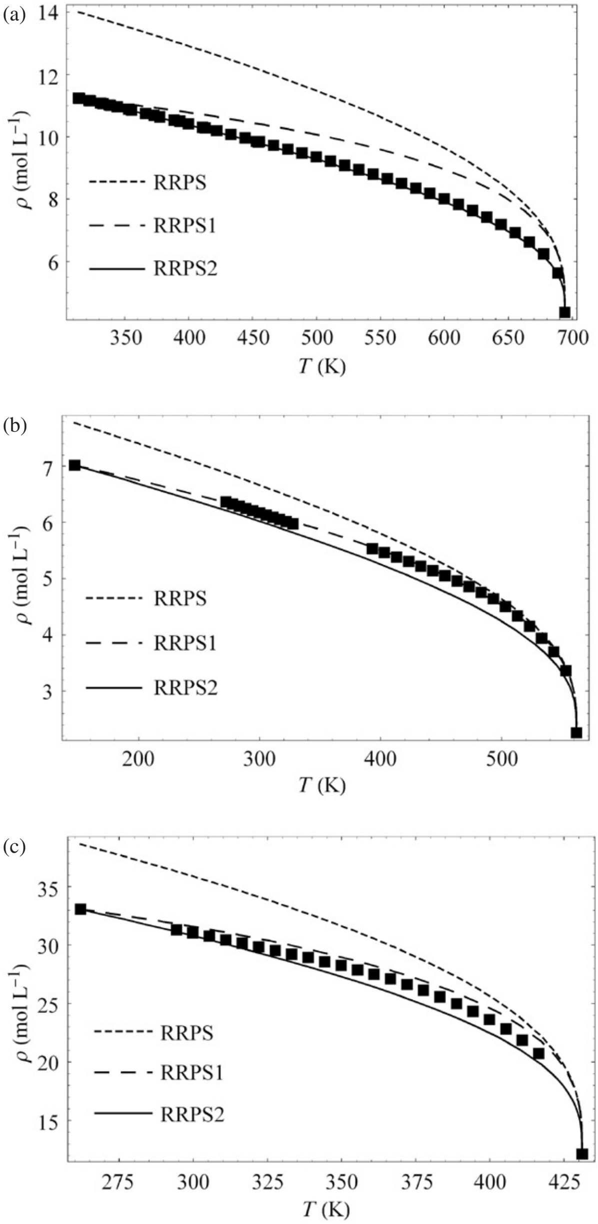

Figure 6. Saturated liquid density *vs*. temperature for (a) phenol, (b) 3,3-dimethylhexane, and (c) nitrogen dioxide. Lines: RRPS, RRPS1, and RRPS2 predictions; points: DIPPR accepted data [28].

It is clear that the new RRPS1 and RRPS2 models give better overall accuracy than the original RRPS model. Moreover, we have observed that the two new models behave similarly, and only for some specific fluids does the choice of one or the other model lead to clearly different results. Thus for several fluids, such as tethrachloroethylene, indole, propionitrile, and phenol (figure 6a), the RRPS2 model gives clearly better

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results than the RRPS1 one, while for some other fluids, such as sodium chloride, nitric oxide, and 3,3-dimethylhexane (figure 6b), the contrary is the case. Finally, we found that for a few fluids, such as water and nitrogen dioxide (figure 6c), the new models cannot reproduce the experimental data adequately.

The most recent model for the saturation liquid density that uses the corresponding states principle and involves no adjustable coefficients for each fluid was proposed by McHaweh *et al.* [11], based on an earlier proposal of Nasrifar and Moshfeghian [14]. The proposed model requires an adjustable coefficient for each fluid to significantly improve the accuracy of the models. For the purpose of comparison with other predictive models, we shall use McHaweh *et al.*'s [11] model but without including that adjustable coefficient, with the critical temperature and density and the acentric factor being the required inputs. Following their notation, we denote this model the simplified-Nasrifar-Moshfeghian-0 (SNM0) correlation. Its analytical expression is

$$\rho = \rho_{\mathrm{C}}\left(c_1 + c_2\tau^{1/3} + c_3\tau^{2/3} + c_4\tau + c_5\tau^{4/3}\right), \tag{7}$$

where the coefficients c_i take fixed values

$$\begin{aligned} c_1 &= 1 \\ c_2 &= 1.169 \\ c_3 &= 1.818 \\ c_4 &= -2.658 \\ c_5 &= 2.161 \end{aligned} \tag{8}$$

and τ is a temperature dependent variable defined by

$$\tau = 1 - \frac{(T/T_{\mathrm{C}})}{\left[1 + m\left(1 - \sqrt{T/T_{\mathrm{C}}}\right)\right]^2} \tag{9}$$

with m being defined as in the Soave-Redlich-Kwong equation of state

$$m = 0.480 + 1.574\omega - 0.176\omega^2. \tag{10}$$

The accuracy of SNM0 has been checked in McHaweh *et al.* [11] and also in Mulero *et al.* [23,24,27]. We have found that this model gives good results for a large number of fluids of different kinds [23,24], but, for some of them is not accurate near the triple point [27].

Following the same procedure as used with the previous models, by taking as reference the triple point density and temperature, we can define new models by changing the value of each of the c_i coefficients, except for the first that must be equal to unity to ensure that the critical density is reproduced. We have also tried to change the m coefficient, but no analytical expression can be found, and only numerical calculations can be made. Moreover, for some fluids we have found convergence problems, and for others the results were clearly wrong. We thus define four new models by changing only one coefficient c_i ($i = 2, \ldots, 5$) and maintaining the values of the others, denoted SNM02, ..., SNM05, as follows:

$$\text{SNM02: } c_2 = \frac{\rho_{\mathrm{T}}/\rho_{\mathrm{C}} - \left(1 + 1.818\tau_{\mathrm{T}}^{2/3} - 2.658\tau_{\mathrm{T}} + 2.161\tau_{\mathrm{T}}^{4/3}\right)}{\tau_{\mathrm{T}}^{1/3}} \tag{11}$$

$$\text{SNM03: } c_3 = \frac{(\rho_{\mathrm{T}}/\rho_{\mathrm{C}}) - \left(1 + 1.169\tau_{\mathrm{T}}^{1/3} - 2.658\tau_{\mathrm{T}} + 2.161\tau_{\mathrm{T}}^{4/3}\right)}{\tau_{\mathrm{T}}^{2/3}} \tag{12}$$

$$\text{SNM04: } c_4 = \frac{(\rho_{\mathrm{T}}/\rho_{\mathrm{C}}) - \left(1 + 1.169\tau_{\mathrm{T}}^{1/3} + 1.818\tau_{\mathrm{T}}^{2/3} + 2.161\tau_{\mathrm{T}}^{4/3}\right)}{\tau_{\mathrm{T}}} \tag{13}$$

$$\text{SNM05: } c_5 = \frac{(\rho_{\mathrm{T}}/\rho_{\mathrm{C}}) - \left(1 + 1.169\tau_{\mathrm{T}}^{1/3} + 1.818\tau_{\mathrm{T}}^{2/3} - 2.658\tau_{\mathrm{T}}\right)}{\tau_{\mathrm{T}}^{4/3}} \tag{14}$$

where τ_{T} is given by equation (9) with $T = T_{\mathrm{T}}$.

All these new models require the temperature and density at both the critical and the triple points, as well as the acentric factor. All of them have four fixed coefficients and two variable (i.e. different for each fluid) coefficients (m and one of the c_i's). Examples of the behaviour of the old and new models are shown in figure 7. One can see that for some fluids the choice of one or another model can lead to clearly different results (figures 7a and b), and that sometimes none of the new models exactly match the data over the whole temperature range (figure 7c), it being difficult to choose the most suitable model. It is therefore necessary to make an overall statistical study of the accuracy of the models for a large number of fluids.

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We have recently proposed a new simple model for predicting both the vapor and the liquid densities of fluids at vapor–liquid equilibrium [27]. The model is based on considering the temperature derivatives of the two densities, and applying the rectilinear diameter law. By fixing the critical exponent at a constant value (1/3), the model involves only two coefficients for each fluid. Both of them have physical meaning and can be calculated straightforwardly from the knowledge of the critical and triple temperatures and densities. The analytical form of the model, which we call here the MPC model, is very similar to that proposed by Reid *et al.*, equation (3):

$$\rho = \rho_{\mathrm{C}} + \alpha(T_{\mathrm{C}} - T) + 3\beta(T_{\mathrm{C}} - T)^{1/3}, \tag{15}$$

where here the coefficients α and β are different for each fluid and have certain physical meanings. First, the coefficient β is related to the slope of the rectilinear diameter, and we have shown that it can be obtained simply from

$$\beta = k\, T_{\mathrm{C}}^{-1/3}\rho_{\mathrm{C}}, \tag{16}$$

where k is a constant that can be obtained from the slope of the rectilinear diameter and the critical temperature and density of a Lennard-Jones fluid. By using the Lotfi *et al.* [30] data ($T_{\mathrm{C}-LJ} = 1.31$ and $\rho_{\mathrm{C}-LJ} = 0.314$, in reduced units) one obtains $k = 0.629885$ [27]. Second, α is obtained by taking into account the rectilinear diameter law and that both the liquid and vapour densities must be equal to the critical density at the critical temperature. By considering that at the triple point the vapour density is significantly less than the liquid density, the coefficient α can be obtained simply from [27]:

$$\alpha = \frac{\rho_{\mathrm{T}} - \rho_{\mathrm{C}}}{T_{\mathrm{C}} - T_{\mathrm{T}}} - 3\beta(T_{\mathrm{C}} - T_{\mathrm{T}})^{-2/3}. \tag{17}$$

Therefore, the proposed model has the same inputs as those considered above and can be compared with them. In our previous work [27] we compared this last model with the SNM0 one. We showed that the present model performs in a similar way for different substances, and gives an adequate qualitative behaviour over the whole temperature range. This was not the case for the SNM0 model, which sometimes underestimated and at other times overestimated the liquid density, and, moreover, seemed to be clearly inadequate for some fluids near the triple temperature.

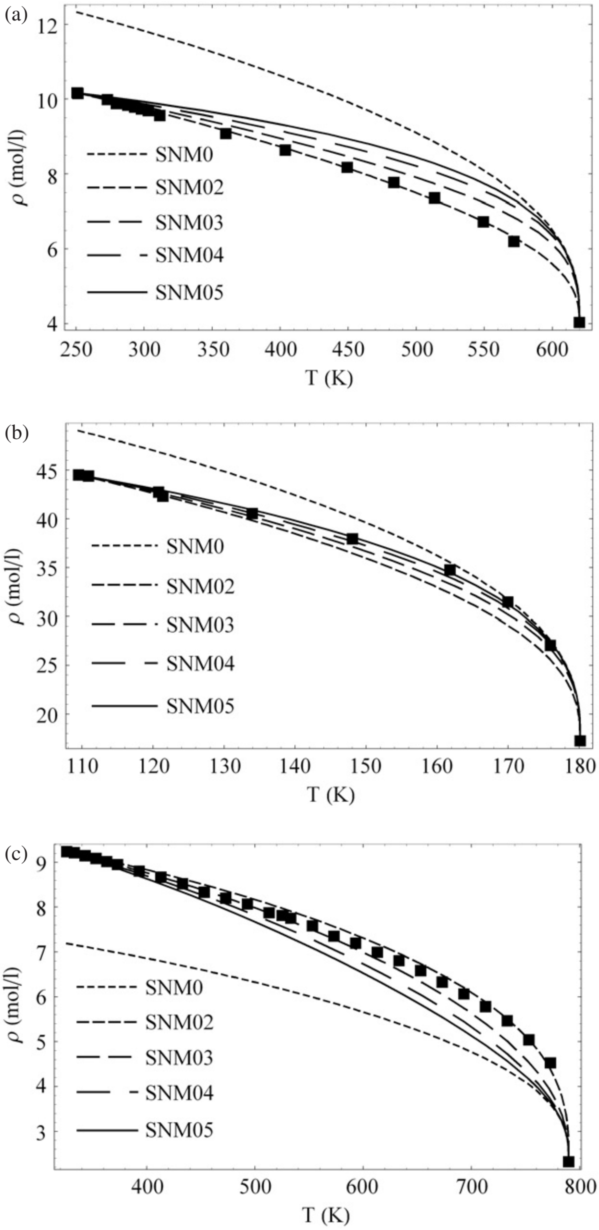

Figure 7. Saturated liquid density *vs*. temperature for (a) tetrachloroethylene, (b) nitric oxide, and (c) indole. Lines: predictions of SNM0 and its modifications; points: DIPPR accepted data [28].

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In our previous work we presented results only for a few selected fluids. In this work we check the accuracy of the new model for a greater number of fluids, and compare it with the other proposed modified models in order to find which is the best general model using both the critical and triple point data as inputs.

3. Results

We calculated the liquid saturation density for 107 fluids by using the original and the modified models proposed here. The values obtained were compared with the data accepted in the DIPPR database [28]. These fluids were selected by taking into account that an adequate number of accepted data are included in the database, and that these data covered a wide temperature range. The input parameters needed (critical and triple temperatures and densities, the critical factor compressibility, and/or the acentric factor) were also obtained from the DIPPR database [28]. A detailed list of fluids and individual results is available upon request.

The results are summarized in table 1, where we give the maximum deviation found for a fluid, the mean absolute average deviation (AAD), and the standard deviation for the 107 fluids selected. As can be seen, the SNM0 model can be considered to be the best original CSP model (i.e., models that use only the critical point data and some other parameter: Z_c or the acentric factor). Nevertheless, the degree of improvement is only low, and indeed a maximum deviation of 50.5% is found for one fluid (sodium chloride).

There is a second group of models that includes SRG [26], RRPS1, the modifications of SNM0, and the MPC recently proposed by us [27]. All of them give AADs below 2.6%. As it can be seen, the SRG model, despite it is less straightforward and contains a larger number of coefficients and input parameters, gives clearly worse results that the other models in this group. We also note that, in this group of models, the MPC is the only one requiring only 4 input parameters, because the others also need the acentric

Table 1. Maximum deviations ($D_{\max}$), mean absolute average deviations (AAD), and standard deviation (SD) for the liquid saturation densities calculated using the models relative to those given by the DIPPR project [28] for 107 fluids. The models are ordered from high to low AADs.

Model	$D_{\max}$ (%)	AAD (%)	SD
Rackett	57.8	4.48	8.34
YG	50.3	3.41	6.13
RRPS	49.9	3.35	6.17
SNM0	50.5	3.09	5.75
SRG	32.3	2.45	5.33
SNM02	10.3	1.66	1.35
MPC	8.3	1.46	1.21
SNM03	6.0	1.33	1.00
SNM05	6.8	1.26	1.16
SNM04	5.6	1.24	1.01
RRPS1	7.1	1.09	1.30
RRPS2	8.5	0.98	1.16
m-Rackett	4.7	0.87	0.90

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factor for each substance. Moreover, it is the only one containing coefficients with a definite physical meaning.

Our results also indicate that, at least for the fluids considered here, better overall results are obtained by modifying the classical Racket and RRPS model than by modifying the more recent SNM0 one. In fact, the RRPS2 and m-Rackett models give clearly the best results, with AADs below 1%. Moreover, the m-Rackett model gives a lower standard deviation, and therefore more homogenous results.

Figure 8 shows the percentage of fluids for which several of these models give AADs less than some fixed values. The curves confirm our previous conclusions. Thus, the models based on the SNM0 proposal give AADs less than 0.5% only for less than 20% of the 107 fluids, whereas for the models based on the Rackett or RRPS modifications this is so for more than 40% of the fluids.

As can be seen in the previous figure, our MPC model and some modifications of the SNM0 model give AADs less than 2% for almost 80% of the fluids, as the m-Rackett and RRPS modifications do. Finally, this figure shows that the m-Rackett model always gives the greatest percentage of fluids for every AAD. If one takes into account that the m-Rackett model is somewhat simpler than RRPS2, and that it always gives individual deviations below 5% and a standard deviation less than 1%, one must conclude that this is the best overall model for the prediction of the saturation density when the triple and critical point data are used as inputs.

We must note that obviously the degree of improvement obtained with the use of the new models can change from one fluid to another. Thus, for example, for sodium chloride the classical models give AADs greater than 49%, whereas for both the RRPS1 and the MPC models the deviation is only 0.5%. For some other substances we found that there is no clear improvement when the new models are used. Thus, for example, for water (figure 9) only the Rackett model can reproduce the saturation liquid density, and then only near the critical point.

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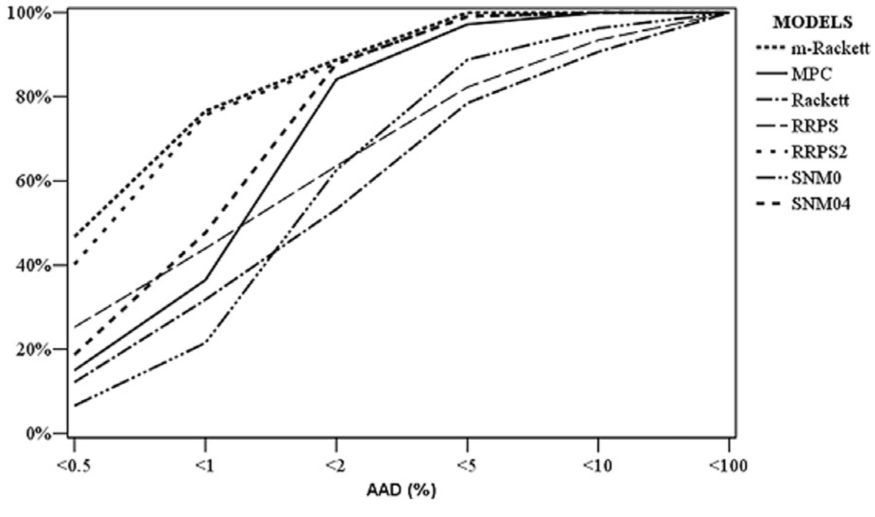

Figure 8. Percentage of fluids for which various of these models (Rackett, m-Rackett, RRPS, RRPS2, SNM0, SNM04, and MPC) give AADs less than some fixed values.

Finally, it is interesting to see how the new models behave for several families of fluids. As one observes in table 2, the classical models give good accuracy for the families considered, but the modified models are clearly better. In particular, the m-Rackett model gives the lowest mean deviation for 10 *n*-alkanes, 9 alkenes, and 11 C–H–F compounds, with the modified RRPS and some modified SNM0 models also giving very good results. RRPS1 gives clearly the lowest AAD for 9 other alkanes (an example is shown in figure 6b). It also gives excellent results for 9 alkylbenzenes, but the RRPS2 and m-Rackett models also give very good results and needed one input parameter less.

For the 7 inorganic gases considered, the SNM04 or SNM05 models give the best results, whereas the classical models give the worst. Finally, it is shown in table 2, that the MPC model, which does not use adjustable coefficients, give adequate results for these families of fluids, whereas the SRG model, which uses 10 fixed coefficients and requires one additional input property, cannot be used with accuracy for inorganic gases.

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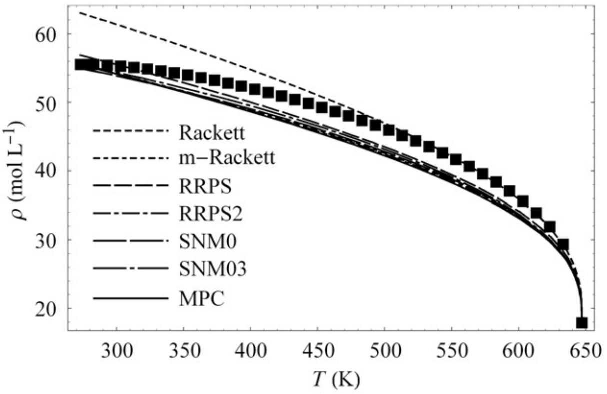

Figure 9. Saturated liquid density *vs*. temperature for water. Lines: predictions of models; points: DIPPR accepted data [28].

Table 2. Mean absolute average deviations (%) for several families of fluids.

Family	*n*-alkanes	Other alkanes	Alkenes	Alkyl-benzenes	C–H–F compounds	Inorganic gases
N	10	9	9	9	11	7
Rackett	1.72	3.33	2.41	1.33	1.77	3.79
m-Rackett	0.50	1.08	0.41	0.51	0.53	1.00
YG	1.39	2.37	1.12	1.13	2.08	4.03
RRPS	1.62	2.96	0.78	0.67	2.05	4.32
RRPS1	0.83	0.53	0.47	0.44	0.87	1.17
RRPS2	0.69	1.87	0.46	0.51	0.59	1.21
SNM0	1.14	1.89	1.23	2.32	2.36	2.45
SNM02	1.62	1.44	1.62	1.82	1.00	1.25
SNM03	1.26	1.07	1.12	1.43	0.76	0.76
SNM04	1.07	1.00	0.87	1.19	0.86	0.55
SNM05	0.96	1.03	0.73	1.04	1.04	0.55
SRG	1.04	1.72	0.51	0.82	0.69	3.85
MPC	1.02	1.19	0.62	1.18	1.41	0.94

N = number of fluids

We would like to remark that the application of the new models requires the knowledge of the density at a reference temperature, and that we have chosen here to use the triple point data for that reference. The triple point temperature is accurately known for the vast majority of substances, but the triple point density is not always available or is often inaccurate because of the experimental difficulties in measuring it at very low pressures. In any case, we note that the new models, including that proposed recently by us, can be used by taking as reference the value of the density at any other temperature, giving then good results for higher temperatures [27]. A clear example is shown in figure 10, where the m-Rackett model is used with different reference temperatures.

4. Conclusions

Seven new models to predict the liquid saturation density of pure fluids were here proposed. All of them are simple modifications of classical models based on the corresponding states principle. In each case, the modification consists in changing a coefficient in order to ensure that the model reproduces exactly the density at the triple point. All the new proposed models require, therefore, the critical and triple point temperatures and densities. Moreover, five of them also require the acentric factor as input.

Results for 107 fluids of different kinds were obtained by using the original classical models, the modified models proposed here, a model based on a scale-variable-reduced-coordinate framework, and also a model recently proposed by us. This last model contains only two variable coefficients with a definite physical meaning, and that also depend on the temperature and density at both the critical and the triple points. All the modified models and our recent model can be used to also predict the vapour density by using the rectilinear diameter law, without needing additional inputs. Moreover, these models can be used by taking as reference a point on the vapor–liquid saturation curve different from the triple point.

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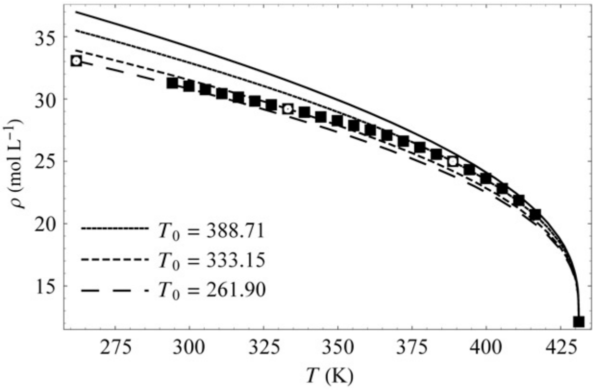

Figure 10. Saturated liquid density *vs*. temperature for nitrogen dioxide. Full line: prediction of the original Rackett model. Dashed line: prediction of the m-Rackett model using different reference temperatures (white circles); points: DIPPR accepted data [28].

Our results indicate that the new models clearly improve the estimates in the whole temperature range with respect to the classical CSP ones and some others using the triple point as reference. Indeed, we showed that a simple modification of the well-known and straightforward Rackett model gives an excellent overall accuracy (mean average absolute deviation 0.9%) for the fluids considered.

Results for six representative families of fluids were also obtained. They indicate that the modified Rackett model gives excellent results for *n*-alkanes, alkenes, alkylbenzenes, and C–H–F compounds. Nevertheless, for other alkanes and for inorganic gases other models slightly improve the overall results obtained with the modified Rackett model.

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