Fundamental equation of state for R1234yf

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Abstract. Unified fundamental equation of state for R1234yf has been developed that satisfies the scaling critical point theory. It has been demonstrated that the proposed equation of state truly represents the peculiarities of the thermodynamic surface from the qualitative and quantitative point of view: first, in the regular part of the thermodynamic surface, secondly, in the region of strongly developed density fluctuations. The operating range of the equation of state has been determined on the basis of the benchmarking analysis with experimental and estimated data: for temperature $230 \leq T \leq 420$ K; for pressure $0.001 < p < 20$ MPa.

1. Introduction
Substance 2,3,3,3-tetrafluoropropene (R1234yf) relates to a group of fluorinated hydrocarbons [1]. At the present time it is proposed to replace R134a in automobile air conditioners and other applications [2]. In normal conditions the R1234yf is a stable material with low toxicity which relates to the class of barely flammable refrigerants. In terms of safety the R1234yf is awarded classification A2L as per the ASHRAE standard. The data on the thermodynamic properties of R1234yf [3–11] and the equation of state (EOS) [10–14] developed on the basis of this equation have appeared in open literature quite recently. Hereby, the fundamental equations of state (FEOS) [10–14] do not express the peculiarities of the thermodynamic surface even qualitatively within the neighborhood of the critical point. Therefore, we cannot classify the FEOS [10–14] as unified fundamental equations of state (UFEOS). In fact, the UFEOS’s are referred to the equations of state which in the regular parts of the thermodynamic surface turn into the virial equations of state, while within the asymptotic neighborhood of the critical point they are transformed into the scaled Widom equation [15]. At the same time the works [16–18] propose a method of UFEOS formulation as exemplified by examples of building of R134a [19], R236ea [20], R32 [21] and R218 [22].

Therefore, in order to describe the equilibrium properties we have developed R1234yf UFEOS on the basis of a critical point phenomenological theory [16] which is based on the method of pseudocritical points [23].

2. UFEOS Structure
While building R1234yf UFEOS we have decided to confine ourselves to the simplest model. Therefore, let us choose the Helmholtz free energy expression $F(\rho, T)$ as initial expression for
the UFEOS in accordance with [16, 20]; this structure includes only one scaling function \( a(x) \) of free energy:

\[
F(T, \rho) = F_0(T, \rho) + RT \omega \sum_{i=0}^{14} \sum_{j=0}^{3} (C_{i,j} \tau_i^j \Delta \rho^j) + RT_c f|\Delta \rho|^\delta a(x),
\]

where \( F_0(T, \rho) \) is an ideal gas component of free energy; \( C_{i,j} \) are constant coefficients; \( \tau_i = T_c/T - 1 \); \( x = \sigma/|\Delta \rho|^{1/\beta} \); \( \tau = T/T_c - 1 \); \( \omega = \rho/\rho_c \); \( \Delta \rho = \omega - 1 \); \( \beta \) and \( \delta \) are critical indices; \( \rho_c \) and \( T_c \) are critical parameters; \( R \) is the gas constant.

In the UFEOS (1) the scaling function of the Helmholtz free energy \( a(x) \) is determined by expression [24]:

\[
a(x) = A \left( (x + x_1)^{2-a} - \varepsilon(x + x_2)^{2-a} \right) + B(x + x_3)^\gamma + C,
\]

where \( A = -\Gamma k \gamma_1/[2ab^2 \alpha_1 (1 - \varepsilon)] \); \( B = \Gamma (2k)^{-1} \); \( \alpha_1 = (\alpha - 2)(\alpha - 1) \); \( \gamma_1 = \gamma(\gamma - 1) \); \( \varepsilon = x_1/x_2 \);

\( b^2 = (\gamma - 2\beta)/[\gamma(1 - 2\beta)] \); \( k = [(b^2 - 1)/x_0] \); \( C \) is the constant which we find in the equality [22]: \( (2 - \alpha)a(x = -x_0) - x a'(x = -x_0) = 0 \); \( \Gamma \) is the individual parameter.

The choice of the Helmholtz free energy in the form of (1) first of all, essentially simplifies the search algorithm of the parameters of the fundamental EOS (1) secondly, as shown in the works [16, 20] the structure (1) is computed on the basis of the experimentally confirmed Benedek hypothesis [25] and the critical point phenomenological theory [26].

Let us select a cross-over function in the form of [21]:

\[
f = \exp \left[ -a(\Delta \rho)^2/\omega^b \right],
\]

where \( a \) and \( b \) are constant parameters.

Such choice of a crossover function permits, first of all, in the region of small densities and pressures to pass over to (1) to the virial equation:

\[
Z = 1 + \omega B(T) + \omega^2 C(T) + ..., \quad (4)
\]

where \( Z = p/(\rho RT) \) represents compressibility; \( B(T) \) and \( C(T) \) are the second and the third virial coefficients respectively. Secondly, in the region of strongly developed density fluctuations, let us pass to the Widom equation [15]:

\[
\Delta \mu = \Delta \rho|\Delta \rho|^{\delta-1} h(x),
\]

where \( \Delta \mu \) is the chemical potential function of singularities \( \mu \); \( h(x) \) is the chemical potential scaling function.

3. Choice of scaling function parameters

To calculate parameters \( x_1 \), \( x_2 \), \( x_3 \) of the scaling function (2) we have used a system of equations [24]:

\[
-\frac{(b^2 - 1)^\beta \gamma_1 (2 - \alpha)}{2ab^2 \alpha_1 (1 - \frac{x_4}{\varphi_2})} \left( \frac{\varphi_1^{1-a} - \varphi_1^{1-a}}{\varphi_2^{20}} \right) + \frac{\gamma}{2(b^2 - 1)^\beta} \varphi_3^{\gamma-1}
\]

\[= -\frac{(b^2 - 1)^\beta \gamma_1}{2ab^2 (1 - \alpha)} \left( 1 - \frac{(1 - 2\beta)(1 - \alpha)}{\gamma - 1} \right) (b^2 - 1)^{\alpha-1}, \quad (6)
\]

\[
-\frac{(b^2 - 1)^\beta \gamma_1 (2 - \alpha)}{2ab^2 \alpha_1 (1 - \frac{x_4}{\varphi_2})} \left( \frac{\varphi_1^{1-a} - \varphi_1^{1-a}}{\varphi_2^{20}} \right) + \frac{\gamma}{2(b^2 - 1)^\beta} \varphi_3^{\gamma-1}
\]

\[= -\frac{(b^2 - 1)^\beta \gamma_1}{2ab^2 (1 - \alpha)} \left( 1 - \frac{(1 - 2\beta)(1 - \alpha)}{\gamma - 1} \right) (b^2 - 1)^{\alpha-1} \frac{b(\alpha - 1)/\beta}{}, \quad (7)
\]
- (δ + 1) (b^2 - 1)^{\beta} \gamma_1 \left( \varphi_{1}^{2-\alpha} - \varphi_{10}^{2-\alpha} - \varphi_{10}^{-1-\alpha} - \frac{\varphi_1}{\varphi_2} (\varphi_{2}^{2-\alpha} - \varphi_{20}^{2-\alpha} - \varphi_{20}^{-1-\alpha}) \right)

+ \frac{\delta + 1}{2(b^2 - 1)^{\beta}} (\varphi_3^{2-\alpha} - \varphi_{30}^{2-\alpha} - \varphi_{30}^{-1-\alpha}) = \frac{1}{b} \left( 1 - \frac{1}{b^2} \right)^{\gamma} \left( \frac{(b^2 - 1)^{\beta}}{b} \right)^{-\delta},

where \varphi_0 = \varphi_1 - 1; \delta = 1 + \gamma/\beta, \alpha = 2 - (\beta \delta + \beta); x_1 = \varphi x_0, x_4 = \varphi_3 x_0, (i \in 1, 2, 3).

By solving the system of equations (6)–(8) with \beta = 0.3255; \gamma = 1.239 selected in accordance with the Ising model [27] we get the following values for the required parameters: \varphi_1 = 2.80724769, \varphi_2 = 14.4717304, \varphi_3 = 5.73246825.

The values of the \varphi_i parameters are determined only by the critical indices. Hence, the scaling function (2) with the parameters computed on the basis of (6)–(8) describes the thermal spinodal \( \partial p/\partial \rho \) = 0 and, in accordance with the Benedek hypothesis, the line of pseudocritical points [28]: \( \partial T/\partial s \) = 0 \Leftrightarrow \( \partial p/\partial \rho \) = 0.

Our computations have shown that the maximum deviation of the scaling functions calculated on the basis of (2) from the corresponding scaling functions of the Schofield-Litster-Ho linear model (LM) [29] does not exceed 1.0%. This makes it possible for us to conclude that the scaling function (2) with the parameters calculated on the basis of equations (6)–(8) is no less inferior to the LM by its design characteristics and may be recommended for the computation of singularity functions of the scaling and wide-range equations of state.

4. R1234yf UFEAS Structure

With the purpose to satisfy the power functions of the scaled theory [30], it is necessary that the fundamental equation of state satisfies the following requirements:

\((\partial^np/\partial \rho^n)_T = 0 \quad \text{and} \quad (\partial p/\partial \rho)_{\rho=\rho_c,T\rightarrow T_c} = o(\tau),\)

where \(n \in 1, 2, 3, 4\).

In order that the equations (9) be fulfilled, it is sufficient to present the expression for the Helmholtz free energy (1) in the form:

\[ F(T, \rho) = F_0(T, \rho) + RT \omega \sum_{i=0}^{14} \sum_{j=0}^{3} \left( C_{i,j} \tau_i^j \Delta \rho^j \right) + RT \xi |\Delta \rho|^{\delta+1} a(x) \]

\[ + RT \left( \tau_1 (\omega^2 - 3\omega) D_1 + \tau_1 (\omega^3 - 2\omega^2) D_2 + \omega y_2 + \omega y_4 D_3 + \omega y_6 D_4 + \ln(\rho) \right), \]  

where \(y_2 = -15.4/12 + 5.8/12 \Delta \rho - 2.2/12 \Delta \rho^2 + 0.05 \Delta \rho^3; y_4 = 5 - 4 \Delta \rho + 3 \Delta \rho^2 - 2 \Delta \rho^3 + \Delta \rho^4; y_6 = 4 - 3 \Delta \rho + 2 \Delta \rho^2 - \Delta \rho^3 + \Delta \rho^5.\)

The ideal gas component of the Helmholtz free energy for R1234yf is chosen by us [10] in the form of:

\[ F_0(T, \rho) = RT \left\{ a_1 + a_2 T_c/T + 4.944 \ln (T_c/T) \right. \]

\[ + \sum_{i=1}^{4} \nu_i \ln \left[ 1 - \exp (-u_i/T) \right] \left\} \right. \]

where \(a_1 = 30.9602479228, a_2 = -17.8731205385, \nu_1 = 7.549; \nu_2 = 1.537; \nu_3 = 2.030; \nu_4 = 7.455; u_1 = 718.0; u_2 = 877.0; u_3 = 4463.0; u_4 = 1755.0.\)
Table 1. Coefficients $C_{i,j}$ of UFEOS (10).

| $i$ | 0 | 1 | 2 | 3 |
|-----|---|---|---|---|
| 0   | 0 | 0 | 2.1819506716969 | −3.4431250638676 |
| 1   | 0 | 0 | −0.76970699558922 | 6.0958552089629 |
| 2   | 0 | 0 | −5.7335333143687 | −0.9342144538773 |
| 3   | 0 | −1.8689156395437 | 1.6228533578506 | −4.4670251655715 |
| 4   | 0 | 0.8688841041663 | 6.8806754075274 | 3.3085183948727 |
| 5   | 0 | 1.3148738547285 | −2.9483529493783 | −0.69331092411481 |
| 6   | −0.19027489084292 | −3.0308539790982 | −3.5172134509465 | 0 |
| 7   | 0.11866892324563 | 1.0945051720156 | 2.437727291283 | 0 |
| 8   | 0.2027690925539 | 2.3408942891167 | 0 | 0 |
| 9   | −0.21141348357975 | −2.4679066686767 | −0.2270135398263 | 0 |
| 10  | −0.036024435416913 | 0.2739590029156 | 0 | 0 |
| 11  | 0.10747548881033 | 0.87939001526249 | 0.0098923027571363 | 0 |
| 12  | −0.038145872948055 | −0.629564961460868 | 0 | 0 |
| 13  | 0.0010267727264501 | 0.18551156470689 | 0.00029861577234118 | 0 |
| 14  | 0.00105905153298 | −0.021348367687569 | 0 | 0 |

Figure 1. Relative divergence values of density $\delta \rho = (\rho_{\text{exp}} - \rho_{\text{calc}}) / \rho_{\text{exp}} \times 100\%$ calculated as per the equations presented in this study as compared with the experimental and tabular data: 1 – [7], 2 – [7], 3 – [10].

The following values have been appointed to the UFEOS (10) parameters: $x_0 = 0.245$; $T_c = 367.85$ K; $p_c = 3.38249$ MPa; $\rho_c = 475.55$ kg/m$^3$; $R = 72.907$ kJ/(g×K); $a = 2$, $b = 0.183$; $\Gamma = 4.5056106421604$; $D_1 = 0.93900346168214$; $D_2 = 0.7368385361871$; $D_3 = 0.011335254322352$; $D_4 = 0.053879562021166$; coefficients $C_{i,j}$ are presented in table 1.

Within the framework of our approach, the computing formulas have a simple structure. For instance, the computing formula for isochoric heat capacity $C_v$ calculated on the basis of (1) has the following form:

$$C_v(T, \rho) = \frac{-R\omega}{\tau^2} \sum_{i=0}^{14} \sum_{j=0}^{3} C_{i,j} (j-1) \tau_i^{j-2} \Delta \rho^j - R t f |\Delta \rho|^{-\frac{a}{2}} a''(x) + C_0(T), \quad (12)$$
5. Results

We have performed a comparative analysis of values $p$, $\rho$, $T$ for the data, the isobar heat capacity and sound speed calculated as per UFEOS (10) with the corresponding experimental data [3–11]. It is found that the UFEOS (10) expresses with small uncertainty (within the experimental data error range) both the thermal surface and the experimental data about $\rho$ (figure 1), $C_p$ (figures 2 and 3) and $w$ (figure 4). As distinct from FEOS [10], the equation of state (10) forming the basis of the proposed method reflects the behavior of the isochoric heat capacity within the neighborhood of the critical point in accordance with the scaling theory of critical phenomena (figure 5).

For the experimental values $X^{(e)}$ from references [3, 7, 9–11, 31, 34], the absolute deviation

$$C_0(T) = R \left\{ 4.944 + \sum_{i=1}^{4} v_i (u_1/T)^2 \exp \left(-u_i/T\right)/(1 - \exp \left(-u_i/T\right))^2 \right\}.$$  \hspace{1cm} (13)
Figure 4. Relative divergence values of sound speed $\delta w = (w_{\text{exp}} - w_{\text{calc}})/w_{\text{exp}} \times 100\%$ calculated as per the equations presented in this study as compared with the experimental data [3]. Pseudoisothermal lines: 1 – 278.15 K, 2 – 293.15 K, 3 – 308.15 K, 4 – 323.15 K, 5 – 338.15 K, 6 – 353.15 K.

Figure 5. Values of isochoric heat capacity on the isothermal line $T = T_c + 0.0001 K = 367.8501 K$: 1 – calculation as per UFEOS (10), 2 – calculation as per FEOS [10], 3 – critical isochore.

$(\Delta X)$ and percentage deviation $(\delta X)$ are calculated as follows:

$$\Delta X = X^{(e)} - X^{(r)}, \quad \delta X = 100\Delta X/X^{(e)}\%,$$

where $X^{(r)}$ is the value of the equilbrium property $X (X = C_V, X = C_p, \ldots)$ calculated on the basis of UFEOS (10).

For the selected data sets from references [3, 7, 9–11, 31, 34], the following root-mean square deviation $(RMS)$ are defined [35]:

$$RMS = \sqrt{\frac{\sum_{n=1}^{N} (\delta X_n)^2}{N}}.$$
Figure 6. Relative divergence values $\delta p_s = (p_{s,exp} - p_{s,calc})/p_{s,exp} \times 100\%$ calculated as per the equations presented in this study as compared with the experimental and tabular data: 1 – [10], 2 – [4], 3 – [31], 4 – [32], 5 – [33], 6 – [13].

Table 2. Statistical comparison between the UFEOS (10) and the selected measured points from references [3, 7, 9–11, 31, 34].

| $X$ | $\rho$, [7] | $\rho$, [10] | $\rho$, [31] | $C_v$, [11] | $C_p$, [9] | $w$, [3] | $w$, [34] |
|-----|-------------|-------------|-------------|-------------|-------------|----------|----------|
| RMS, % | 0.15 | 0.22 | 0.11 | 1.74 | 0.46 | 0.10 | 0.88 |

The survey of statistical deviations of selected data sets from references [3, 7, 9–11, 31, 34] given in table 2.

It should be noted that for the calculation of the equilibrium properties of R1234yf as per UFEOS (10) within the framework of the proposed methodology, it is required to have an elasticity line equation $p = p_s(T)$. We have developed this equation by the procedure considered in depth in [36]:

$$p_s(T) = p_c \exp \left( -\frac{d_0 \tau^2}{t} \right) \left( 1 + d_1 \tau + d_2 |\tau|^{2-\alpha} + d_3 |\tau|^{2-\alpha+\Delta} + \sum_{i=4}^{6} d_i \tau^{s_i} \right),$$  

where $d_0 = 9.6$; $d_1 = 7.354199461325$; $d_2 = -0.1144693893850$; $d_3 = -68.08539067357$; $d_4 = 50.35509320499$; $d_5 = -26.11051261276$; $d_6 = 2.195507223477$; $s_4 = 2$; $s_5 = 3$; $s_6 = 5$.

The values for coefficients $d_i$ and indices of power $s_i$ which are components of equation (16) are determined on the basis of experimental information [4, 10, 13, 31–33].

The results of comparison with experimental and tabular data on pressure in the elasticity line are presented in figure 6. There is observed good agreement with the data [4, 31] within the neighborhood of the critical point.

Calculated values of properties from the UFEOS (10) to verify computer code: $T = 400$ K, $\rho = 1000$ kg/m$^3$, $p(T, \rho) = 31600.415$ kPa, $C_v(T, \rho) = 1.06128070$ kJ/(kg×K).

6. Summary

The PCP method permits to develop unified fundamental equations of state for substances having various molecular structures. In this study, the PCP method is proved by the example of building of a new alternative refrigerant agent R1234yf that has allowed to develop R1234yf UFEOS which by its computational characteristics is not inferior to FEOS [10, 12–14] in the regular part of the thermodynamic surface. It should be noted that as contrasted with FEOS
[10, 12–14], the proposed R1234yf UFEOS (10) in accordance with the scaling hypothesis reflects all the behavior peculiarities of the equilibrium properties of the R1234yf within the neighborhood of the critical point.

7. Conclusion
Thus, it is shown that within the framework of the considered approach it is possible to develop UFEOS’s which, in the course of computation of equilibrium properties, are capable of replacing the Van der Waals form FEOS’s and scaling equations of state.

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