Description of the liquid-vapor phase equilibrium line of pure substances within the bounds of scale theory based on the Clapeyron equation

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Abstract. On the basis of the Clapeyron equation and the scale theory, expressions are developed for the “apparent” heat of vaporization \( r' = r'(T) \), vapor \( \rho^- = \rho^-(T) \) and liquid \( \rho^+ = \rho^+(T) \) branches of the saturation line of individual substances for the range of state parameters from the triple point \((p_t, T_t, \rho_t)\) to the critical \((p_c, T_c, \rho_c)\). The peculiarity of the proposed approach to the description of the saturation line is that all exponents of the components of the equations \( \rho^- = \rho^-(T) \) and \( \rho^+ = \rho^+(T) \) are universal up to the universality of the critical indices \( \alpha, \beta \) and \( \Delta \). In this case, the order parameter \( \rho = (\rho^+ - \rho^-)/(2\rho_c) \) and the average diameter \( d = (\rho^+ + \rho^-)/(2\rho_c) - 1 \) of the saturation line satisfy the saturation line model \([2,1]\alpha - \beta\), which follows from the modern theory of critical phenomena. The method is tested on the example of describing the phase equilibrium line of refrigerant R1233zd(E) in the range from \( T_t = 195.15 \text{ K} \) to \( T_c = 439.57 \text{ K} \). It is found that in the temperature range \([T_t, T_c]\), the developed system of the mutually consistent equations \( p_t = p_t(T) \), \( r' = r'(T) \), \( \rho^- = \rho^-(T) \) and \( \rho^+ = \rho^+(T) \) allows describing the data on the saturated vapor pressure \( p_t \) and densities \( \rho^- \) and \( \rho^+ \) on the saturation line within the experimental uncertainty of these data.

1. Introduction
Refrigerant R1233zd(E), along with R1224yd(Z) is currently considered as an alternative to refrigerants R245fa and R123 in the organic Rankine cycles \([1,2]\), in centrifugal chillers \([3]\) and bladeless turbines \([4,5]\). The global warming potential (GWP) of R1233yf is 150 times less than the GWP of refrigerant R245fa (GWPR1233zd(E) = 4.5–7), and 10 times less than that of refrigerant R123. R1233zd(E) is environmentally safe, as it has zero ozone depletion potential (ODP = 0). For R123, we have ODP = 0.02 and, in accordance with the Montreal Protocol and the Paris Agreement (2015) \([6]\), after 2019, it is prohibited to put new equipment using R123 and other hydrochlorofluorocarbons into operation \([7]\).

All this has led to increased attention to the study of the thermophysical properties of R1233zd(E) \([8–17]\). Experimental and calculated information on the saturated vapor pressure \( p_t \) \([8–14]\), density...
\( \rho^- < \rho_c \) [15, 16] and \( \rho^+ > \rho_c \) [8, 10–13, 17] on the saturation line allows obtaining a reliable array of initial information for constructing local equations describing the phase equilibrium line in the range from the triple point \((T_T, \rho_T, p_T)\) to critical \((T_c, \rho_c, p_c)\). Along with that, until now, local equations describing the saturated vapor density \( \rho^- = \rho^-(T) \) of R1233zd(E) are absent, and the equations of the elastic line \( p_s = p_s(T) \) and the liquid branch \( \rho^+ = \rho^+(T) \) of the coexistence curve do not satisfy modern ideas [18–20] about the behavior of substance in the critical point vicinity.

When describing the phase equilibrium line, it should be kept in mind that the elasticity line and saturation line are projections of the phase equilibrium line on the planes \( p-T \) and \( \rho-T \), respectively. Therefore, the equations \( p_s = p_s(T) \), \( \rho^+ = \rho^+(T) \) and \( \rho^- = \rho^-(T) \) should be consistent in the following parameters:

a) have the same critical indices \( \alpha \), \( \beta \) and \( \Delta \) in accordance with the scale theory (ST) [18];

b) the coefficients in the equations \( \rho^+ = \rho^+(T) \) and \( \rho^- = \rho^-(T) \), which ensure the behavior of the order parameter \( d_s \) and the average diameter \( d_f \) of the saturation line in accordance with the model 2 \( \beta, 1-\alpha \) \[19, 21\] according to which the scaling parts \( d_{s, \text{scal}} \) of the order parameter and \( d_{f, \text{scal}} \) of the average diameter include a number of leading components \( d_{s, \text{scal}} = a|\tau|^\beta + a|\tau|^{\beta+\Delta} \) and

\[
d_f = c|\tau|^{2\beta} + d|\tau|^{\beta-\alpha} + e|\tau|, \quad \text{where} \quad \tau = \frac{T}{T_c} - 1; \tag{1}
\]

c) the equation \( p_s = p_s(T) \) describes the saturated vapor pressure in accordance with the requirements of ST and has common coefficients with the equation \( \theta^+ = \theta^+(T) \) [22], where \( \theta^+ \) is the "apparent" heat of vaporization.

The purpose of this work is, firstly, to develop a method for constructing a system of equations \( p_s = p_s(T) \), \( \rho^+ = \rho^+(T) \) and \( \rho^- = \rho^-(T) \), satisfying conditions a), b) and c), and, secondly, to test the proposed method by the example of describing the phase equilibrium line of the refrigerant R1233zd(E).

2. Method for calculating the liquid-vapor phase equilibrium line

In the temperature range from \( T_T \) to \( T_c \), in order to match the values of pressure and density of saturated vapor, and density of saturated liquid of the refrigerant R1233zd(E), we employed the system of consistent equations [22–26], which the authors of [22–26] had used in various modifications to calculate the phase equilibrium line of a number of substances: \( SF_6 \) [22, 25], R218 [23, 24] and R1234yf [26].

The system of equations [23–26] is based on the Clapeyron equation:

\[
\frac{dp_s}{dT} = \frac{r}{T(V^- - V^+)}. \tag{2}
\]

Here \( r = \Delta H \) is the heat of vaporization, \( V^- \) and \( V^+ \) are the specific volumes of the phases being in equilibrium; \( \Delta H \) is the difference in the specific enthalpy of the phases being in equilibrium.

Let us use the fact that \( V^- = 1/\rho^- \) and \( V^+ = 1/\rho^+ \), and the heat of vaporization \( r \) is related to the "apparent" heat of vaporization by the dependence: \( r^+ = r / (1 - \rho^- / \rho^+) \), so, we bring the Clapeyron equation (2) to the following form:
\[ \rho^-(T) = \frac{T \, dp}{r \, dT}. \]  

(3)

We have chosen the equation \( p = p_s(T) \) in accordance with the recommendations of [27]:

\[ p_s = \rho c e^{-\frac{b}{T}} \left( 1 + a_1 \tau + a_2 |\tau|^{2-\alpha} + a_3 |\tau|^{2-\alpha+\Delta} + a_4 |\tau|^3 + a_5 \tau^2 \right), \]

(4)

where \( a_i \) are the constant coefficients, \( i \in \{0,1,2,...,5\} \), \( t = T/T_c \), \( \tau = T/T_c - 1 \), \( \alpha \) and \( \Delta \) are the critical indices, \( n(i) \in N \).

We set the function \( r^* = r^*(T) \) in the form of a power dependence:

\[ r^*(T) = \frac{\rho}{\rho_c} \left( d_0 + d_1 |\tau|^\beta + d_2 |\tau|^{\beta+\Delta} + d_3 |\tau|^{2\beta} + d_4 |\tau|^{\beta-\alpha} + d_5 |\tau|^\beta + d_6 |\tau| + \sum_{i=7}^9 d_i |\tau|^\gamma \right), \]

(5)

where \( d_i \) are the constant coefficients.

In order to find the values of the exponents \( \chi_i \) used in (6), we have substituted expressions (4) and (5) in (3):

\[ \rho^- = \rho_c \left[ 1 + D_1 |\tau|^\beta + D_2 |\tau|^{\beta+\Delta} + D_3 |\tau|^{2\beta} + D_4 |\tau|^{\beta-\alpha} + D_5 |\tau| + \sum_{i=6}^{11} D_i |\tau|^\gamma \right], \]

(7)

where \( \chi_i = 1 - \alpha + \beta \); \( \chi_6 = 4 \beta \); \( \chi_9 = 4 \beta + \Delta \); \( \chi_i = 1 - \alpha + \Delta \); \( \chi_i = 1 - \alpha + 2 \beta \); \( \chi_i = 1 + 2 \beta \).

At the same time, we have established that the coefficients \( D = (D_1, D_2, ..., D_6) \) (7) are determined on the basis of the equalities:

\[ D_1 = -\frac{d_1}{a_1}, \quad D_2 = -\frac{d_2}{a_2}, \quad D_3 = \frac{d_2^2 - d_1 a_1}{a_1}, \quad D_4 = -\left( \frac{d_1}{a_1} + (2 - \alpha) \frac{a_2}{a_1} \right), \]

(8)

\[ D_5 = \frac{d_3}{a_1} - 2 \left( \frac{d_2 a_2}{a_1^2} - \frac{d_1}{a_1} \right), \quad D_6 = \left( 1 + \frac{d_2}{a_1} - 2 \frac{a_2}{a_1} \right). \]

(9)

According to modern ideas [19, 28, 29] about the behavior of the average diameter \( d_s = (\rho^* + \rho^-)/2 \rho_c - 1 \) in the vicinity of the critical point, we have:

\[ f_d (T \rightarrow T_c) = a |\tau|^{2\beta} + b |\tau|^{\beta-\alpha} + c |\tau| + o(|\tau|), \]

(10)

where \( a, b \) and \( c \) are the constant parameters; and \( o \) is the Landau symbol [30].

In order to exclude the component \( D_5 |\tau|^\beta \) that is absent in (10) from expression (5) it is sufficient to meet the condition:
\[ d_i = \frac{d_{i1}^3}{a_i} - 2 \frac{d_{i} d_{i2}}{a_i}. \]  

(11)

In this case, in dependence (6), the coefficient \( D_3 \) is equal to zero, and thus we exclude the component with the multiplier \( |\tau|^3 \) from the order parameter and the average diameter.

Now, in order to satisfy (7), the liquid branch equation of the saturation line \( R_{1233zd}(E) \) is chosen in the form of a dependence:

\[ \rho^*(T) = \rho_0 \left( 1 + b_1 |\tau|^\alpha + b_2 |\tau|^\beta + b_3 |\tau|^\delta + b_4 |\tau|^\gamma + b_5 |\tau| + \sum_{i=7}^{12} b_i |\tau|^\xi \right), \]  

(12)

where the coefficients \( b = (b_1, b_2, ..., b_5) \) satisfy the following conditions:

\[ b_1 = -D_1, \quad b_2 = -D_2, \quad b_3 = D_3, \quad b_4 = D_4, \quad b_5 = D_5. \]  

(13)

Thus, in contrast to similar equations considered in [23-26], all exponents of the components of equation (12) are universal up to the universality of the critical indices.

The critical indices \( \alpha = 0.11, \quad \beta = 0.325 \) and \( \Delta = 0.51 \) are determined on the basis of the scale theory [18]. The critical parameters of \( R_{1233zd}(E) \): \( \rho_c = 480.220 \) kg/m\(^3\), \( T_c = 439.57 \) K, \( p_c = 3.6237 \) MPa are selected based on the analysis of papers [9, 10, 17].

The remaining parameters of equations (4), (5) and (12) are shown in tables 1–4.

**Table 1.** Parameters of elasticity line equation (4).

| \( i \) | \( a_i \) | \( i \) | \( a_i \) |
|---|---|---|---|
| 0 | 14.0 | 3 | -48.43229307645213 |
| 1 | 7.667397226166193 | 4 | -14.36287722961259 |
| 2 | 37.03632166986891 | 5 | 12.54101606343225 |

**Table 2.** Parameters of vaporization heat equation (5).

| \( i \) | \( d_i \) | \( i \) | \( d_i \) | \( \eta_i \) |
|---|---|---|---|---|
| 1 | 12.8167970732 | 6 | -60.34609985351563 | - |
| 2 | -2.01064395904541 | 7 | 10268.7187963 | 1.215 |
| 3 | 11.940675347363 | 8 | -41118.5559743 | 1.3 |
| 4 | -259.8955993652344 | 9 | 31205.3173786 | 1.325 |
| 5 | -4.106835680137165 | - | - | - |

**Table 3.** Parameters \( b_1 - b_5 \) of equation (12) calculated by formulas (8), (9) and (13).

| \( i \) | \( b_i \) | \( i \) | \( b_i \) |
|---|---|---|---|
| 1 | 1.6715968529008352 | 4 | 24.76680753686911 |
| 2 | -0.26084470922866587 | 5 | 10.522306363888484 |
| 3 | 1.2369049935212735 | - | - |

**Table 4.** Parameters \( b_1 - b_{12} \) of equation (12).

| \( i \) | \( b_i \) | \( \eta_i \) | \( i \) | \( b_i \) | \( \eta_i \) |
|---|---|---|---|---|---|
| 6 | -28982.1783045 | 1.215 | 9 | 173378.128220 | 1.40 |
| 7 | 424489.617292 | 1.30 | 10 | -38794.1945662 | 1.54 |
| 8 | -538673.464724 | 1.325 | 11 | 8547.53476957 | 1.65 |
Table 5. Deviations from the experimental pressure values $p_i$.

| Authors                | S  | AAD | BIAS | SDV  | RMS  | N  |
|------------------------|----|-----|------|------|------|----|
| Li et al. (2019)       | 0.0216 | 0.160 | 0.160 | 0.137 | 0.210 | 95 |
| Yin et al. (2021)      | 0.0368 | 0.138 | 0.138 | 0.0655 | 0.152 | 18 |
| Mondeijar et al. (2015)| 0.0451 | 0.0854 | 0.0547 | 0.209 | 0.211 | 23 |
| Sakoda et al. (2020)   | 0.0589 | 0.1908 | 0.1908 | 0.0442 | 0.195 | 12 |
| Tanaka (2016)          | 0.2029 | 0.328 | -0.3149 | 0.586 | 0.641 | 11 |

3. Analysis of the results obtained

To assess the accuracy of the proposed saturation line model, we have calculated the following statistical characteristics [31]: S, AAD, BIAS, SDV and RMS (tables 5–7).

Table 6. Deviations from the experimental density values $\rho^–$.

| Authors             | S   | AAD | BIAS | SDV | RMS | N  |
|---------------------|-----|-----|------|-----|-----|----|
| Kondou et al. (2015)| 0.0508 | 0.10705 | -0.0315 | 0.1606 | 0.1524 | 10 |
| Cui et al. (2018)   | 0.0571 | 0.1257 | 0.0397 | 0.1977 | 0.1893 | 12 |

Table 7. Deviations from the density values $\rho^+$.

| Authors          | S   | AAD | BIAS | SDV | RMS | N  |
|------------------|-----|-----|------|-----|-----|----|
| Tanaka (2016)    | 0.0154 | 0.03667 | -0.00093 | 0.0511 | 0.0487 | 11 |
| Cui et al. (2018)| 0.007401 | 0.01901 | 0.001403 | 0.418 | 0.0245 | 12 |
| Kondou et al. (2015)| 0.02294 | 0.05456 | 0.05016 | 0.04968 | 0.0688 | 10 |
| Hulse et al. (2012)| 0.02296 | 0.04399 | 0.00093 | 0.0821 | 0.0795 | 13 |

We have found out to what extent the obtained values of the coefficients $D_j = D_{j\beta}$, $D_\alpha = D_{\alpha-a}$ and $D_\kappa = D_{\kappa}$ agree with the values of the corresponding coefficients used in the scaling part of the average diameter $[32]$, $d_{f, scale} = D_{2\beta} |\tau_{\beta}^{2\beta} + D_{1-a} |\tau_{1-a}^{1-a} + D_\alpha |\tau_\alpha|$, obtained by other researchers.

In our case, $E = D_{2\beta} / D_{1-a} = 0.0499$ and $\Omega = D_{2\beta} / D_\alpha = 0.117$. In $[33]$, for H$_2$O, $E = 0.017$, for CH$_3$OH, $E = 0.035$, for R347mcc, $E = 0.073$; in $[34]$, for H$_2$O, $E = 0.128$. Along with that, for a number of substances in $[27, 33]$, the values of $E < 0$ were obtained. For example, in $[27]$, the following limits are set for the parameters $E$ and $\Omega$: $-0.26 \leq E \leq -0.14$ and $0.12 \leq \Omega \leq 0.29$. In our case, the parameter $\Omega = D_{2\beta} / D_\alpha$ is 0.112, which is in satisfactory agreement with the results of $[27]$. From our point of view, some discrepancy in $\Omega$ is explained by different values of the critical indices $\alpha$ and $\beta$. In $[27]$, the following values are accepted: $\alpha = 0.165$ and $\beta = 0.306$, and in this work $\alpha = 0.11$ and $\beta = 0.325$. In contrast to the authors of $[27]$, we have used the theoretical values of the critical indices calculated by the renormalization group method $[18]$.

4. Summary

The system of mutually consistent equations (4), (5), (6) and (12) has the following characteristics:

– with small uncertainty, corresponding to the accuracy of the initial experimental information $[8–17]$, it describes the line of phase equilibrium of R1233zd(E) in the temperature range from $T_c = 195.15$ K to $T_L = 439.57$ K;
– the average diameter $d_f$ and the order parameter $d_\kappa$ calculated on the basis of equations (6) and (12) satisfy the modern theory of critical phenomena $[19, 20]$;
coefficients $D_3 = D_{2\beta}$, $D_4 = D_{s-\alpha}$ and $D_6 = D_t$ are consistent with the values of the corresponding coefficients used in the scaling part of the average diameter $d_{f \text{scale}} = D_{2\beta}|\tau^0| + D_{s-\alpha}|\tau|^{\alpha} + D_t|\tau|$ and obtained by other researchers [27, 32–34].

**Conclusions**

The system of equations (4), (5), (6), and (12) satisfies the requirements of the scale theory of the critical point and can be recommended for calculating pressure $p_*$, heat of vaporization $r$, density $\rho^-$ and $\rho^+$ of individual substances on the phase equilibrium line in the temperature range from the triple point to the critical point.

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