The curvature of the liquid–vapor reduced pressure curve and its relation with the critical region

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\textbf{A B S T R A C T}

For most fluids, there exist a maximum and a minimum in the curvature of the reduced vapor pressure curve, \( p_v = p_v(T) \) (with \( p_v = p/p_c \) and \( T_r = T/T_c \), \( p_c \) and \( T_c \) being the pressure and temperature at the critical point). By analyzing National Institute of Standards and Technology (NIST) data on the liquid-vapor coexistence curve for 105 fluids, we find that the maximum occurs in the reduced temperature range 0.5 \( \leq T_r \leq 0.8 \) while the minimum occurs in the reduced temperature range 0.980 \( \leq T_r \leq 0.995 \). Vapor pressure equations for which \( d^2 p_v/dT_r^2 \) diverges at the critical point present a minimum in their curvature. Therefore, the point of minimum curvature can be used as a marker for the critical region. By using the well-known Ambrose–Walton (AW) vapor pressure equation we obtain the reduced temperatures of the maximum and minimum curvature in terms of the Pitzer acentric factor. The AW predictions are checked against those obtained from NIST data.

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1. Introduction

Some years ago, Srinivasan\textsuperscript{[1]} proposed the study of the curvature (inverse of the radius of curvature) as a way of characterizing the reduced vapor pressure curve. This curvature is defined as

\[ k = \frac{d^2 p_v}{dT_r^2} \left[ 1 + \left( \frac{dp_v}{dT_r} \right)^2 \right]^{-3/2} \]

where \( p_v = p/p_c \), is the reduced vapor pressure and \( T_r = T/T_c \), the reduced temperature, \( p_c \) and \( T_c \) being the pressure and temperature at the critical point. The derivatives appearing in equation (1) can be experimentally obtained from the Clapeyron equation

\[ \frac{p_v}{T_r} \frac{dp_v}{dT_r} = \frac{\Delta h}{T_r (v_g - v_l)} \]

and the Yang–Yang equation\textsuperscript{[2]}

\[ \frac{p_v}{T_r} \frac{d^2 p_v}{dT_r^2} = \frac{d^2 p}{dT^2} \frac{\Delta h}{T (v_g - v_l)} \]

where \( \Delta h \) is the specific enthalpy of vaporization, \( v_g \) and \( v_l \) are the vapor (g) and liquid (l) specific volumes at saturation, and \( c_{v_g} \) and \( c_{v_l} \) are the two-phase vapor and liquid specific heat capacities at constant volume. Alternatively, the first and second derivatives of the reduced vapor pressure can be obtained from vapor pressure data either numerically or from a given functional form of the vapor pressure equation.

By analyzing vapor pressure data of 17 fluids consisting of several refrigerants, carbon dioxide, cryogenic liquids and water, Srinivasan\textsuperscript{[1]} observed the existence of a maximum in the curvature (1) for all the considered fluids (except carbon dioxide), in the reduced temperature range 0.6 \( \leq T_r \leq 0.7 \). Furthermore, Srinivasan\textsuperscript{[1]} also observed the existence of a minimum in the curvature (1) near the critical point for most, but not for all, of the considered fluids. Practical implications of these features for the choice of working fluids in vapor pressure thermometry and in sensor bulbs of the thermostatic expansion valves used in engineering systems were also discussed by Srinivasan in his work\textsuperscript{[1]}.

In the present work we extend Srinivasan’s study by analyzing the curvature of the vapor pressure curve by using liquid-vapor coexistence data for 105 pure fluids reported by the National Institute of Standards and Technology (NIST) program ReProp. 9.0\textsuperscript{[3]}. This extension allows us to enlarge the range for the reduced temperature of the maximum curvature reported by Srinivasan and to show that this reduced temperature is well-correlated with the Pitzer acentric factor \( \omega \). We also analyze the occurrence of a minimum in the curvature of the reduced vapor pressure curve close to the critical point. Indeed, this minimum occurs in the reduced temperature range 0.980 \( \leq T_r \leq 0.995 \), but some of the considered
fluids do not present this minimum. However, by analyzing theoretically the curvature (1) near the critical point we conclude that this minimum must exist for any fluid. This implies that this minimum can be observed only when a thermodynamically consistent vapor pressure equation is chosen. We analyze the case of the Ambrose–Walton vapor pressure equation as a paradigmatic equation in the Pitzer corresponding-states scheme.

2. Curvature far the critical point

Far enough the critical point one can assume that $\Delta_h \approx \text{const}$ and $v^4 \ll v^6 \approx RT/p$. Under these assumptions, by taking as reference the acentric point ($T_r = 0.7$), integration of equation (2) leads to the Clausius–Clapeyron (CC) equation [4]

$$\ln p_r = A(\omega) \left( \frac{1}{T_r} - 1 \right),$$

with

$$A(\omega) = \frac{7}{3} \ln 10 \left( 1 + \omega \right),$$

where $\omega$ is the so-called Pitzer acentric factor defined by Pitzer et al. [5]

$$\omega = -1.0 - \frac{\ln p_r}{T_r} \text{ at } T_r = 0.7.$$  

From equation (4), one obtains

$$\frac{dp_r}{dT_r} = \frac{A(\omega)}{T_r^2} p_r,$$

and

$$\frac{d^2 p_r}{dT_r^2} = \frac{A(\omega)}{T_r^2} \frac{2}{T_r^2} A(\omega) + \frac{\ln p_r}{T_r}.$$  

with $p_r$ given by equation (4). Figure 1(a) and (b) show, respectively, the first and second derivatives of the reduced vapor pressure for propane. Symbols correspond to equations (2) and (3) with $\Delta_h$, $v^4$, $v^6$, $C_{v2}$ and $C_{v3}$ data obtained from RefProp 9.0 [3]. Dashed lines correspond to equations (7) and (8) with $\omega = 0.1521$, the value of the acentric factor for propane [3]. One can see that the CC equations (7) and (8) reproduce fairly well the NIST data far away from the critical point.

Substitution of equations (7) and (8) into equation (1) yields

$$k_{CC} = \frac{A(\omega) p_r T_r^2}{A(\omega) - 2 T_r + \frac{\ln p_r}{T_r} \left( T_r^2 + A(\omega) \frac{\ln p_r}{T_r} \right)^{1/2}}.$$  

for the curvature of the CC equation. The curvature for propane in the range $0.3 \leq T_r \leq 0.95$ using equation (9) with $\omega = 0.1521$ is plotted in figure 2(a) by a dashed line, showing a maximum at $T_{r,\text{max}} = 0.6543$. Figure 2(a) also shows (symbols) the curvature for propane using equations (1)–(3) and $\Delta_h$, $v^4$, $v^6$, $C_{v2}$ and $C_{v3}$ data obtained from RefProp 9.0, in the reduced temperature range $0.3 \leq T_r \leq 0.95$. This curvature presents a maximum at $T_{r,\text{max}} = 0.6505$, close to the value obtained by means of the CC equation. This agreement is due to the fact that the value of $T_{r,\text{max}}$ is far from the critical point and near the acentric point ($T_r = 0.7$) chosen as reference to write the CC equation in the form of equation (4).

Using equations (1)–(3), we have analyzed the curvature of the 105 substances included in RefProp 9.0 and listed in table 1, in the reduced temperature range from $T_{r,\text{top}} = T_\Theta/T_c$ to $T_r = 0.95$, $T_\Theta$ being the triple-point temperature. For each fluid, the curvature presents a maximum at a different reduced temperature $T_{r,\text{top}}$ reported in the third column in table 1. The curvature for CO$_2$, cyclopropane, propyne and SF$_6$ does not present a maximum. In the cases of CO$_2$, SF$_6$, this absence is because their triple point reduced temperature is larger than 0.7. In the cases of cyclopropane and propyne the absence of a maximum in the curvature comes from numerical problems with the data reported in RefProp 9.0 for these fluids [3].

Figure 3(a) shows a plot of $T_{r,\text{max}}$ vs. $\omega$. Symbols correspond to NIST data using the third column in table 1 and the dashed line corresponds to the maximum of the curvature of the CC vapor pressure equation, given by equation (9). We can see a fair agreement between NIST and CC values of $T_{r,\text{max}}$. The average absolute relative deviation (AARD) between NIST and CC data for all fluids is 0.72%. The maximum absolute relative deviation (MARD) is obtained for MDM3M with a value of 1.47%.

Perhaps, the most widely recognized vapor pressure equation used in the literature for correlating vapor pressure experimental data of pure fluids with very good accuracy from the triple to the critical point is the Ambrose–Walton (AW) equation [6].

$$\ln p_r = \phi_0(T_r) + \omega \phi_1(T_r) + \omega^2 \phi_2(T_r),$$

where the functions $\phi_k(T_r)$ ($k = 0, 1, 2$) have the form of a Wagner vapor pressure equation

$$\phi_k(T_r) = \frac{1}{T_r} \left[ A_k(1 - T_r) + B_k(1 - T_r)^{1.5} + C_k(1 - T_r)^{2.5} + D_k(1 - T_r)^5 \right],$$

where the twelve coefficients $A_k$, $B_k$, $C_k$ and $D_k$ ($k = 0, 1, 2$) take the same values for any fluid and are given in table 2. From equations (10) and (11) one obtains

![Figure 1](image.png)

**Figure 1.** (a) Plot of the first derivative of the reduced vapor pressure $dp_r/dT_r$ vs. the reduced temperature $T_r$ for propane. (b) Plot of the second derivative of the reduced vapor pressure $d^2p_r/dT_r^2$ vs. $T_r$ for propane. The solid lines represent equation (12) in (a) and equation (13) in (b), the dashed lines represent equation (7) in (a) and equation (8) in (b), in all cases $\omega = 0.1521$. The symbols are the values obtained from RefProp 9.0 [3] (see text).
The first and second derivatives of the reduced vapor pressure for propane (ω = 0.1521) using equations (12) and (13) are plotted by solid lines in figure 1(a) and (b), respectively. One can see an excellent agreement between NIST and AW results.
For example, for the AW equation (10), using equations (12) and (13), is also plotted in figure 2(a) by a solid line in the first and second derivatives of the AW equation, given by equations (12) and (13), is also plotted in figure 2(a) by a solid line in the inset of figure 3(a). The AARD between NIST and AW data of 4.49%. We ascribe this deviation to the lack of accuracy of the relative deviations (102). The MARD is obtained for 4He with a value of 0.94%. This curvature presents a maximum at $T_{\text{max}} = 0.6507$, very close to the value obtained from NIST data. The reduced temperature of the maximum of the curvature of the AW vapor pressure equation vs. $\omega$ is also plotted in figure 3(a) by a solid line. We can see an excellent agreement between NIST and AW values of $T_{\text{max}}$, except for 4He. Percent relative deviations (102) between NIST and AW data are shown in the inset of figure 3(a). The AARD between NIST and AW data for all fluids is 0.17%. The MARD is obtained for 4He with a value of 4.49%. We ascribe this deviation to the lack of accuracy of the AW equation for the vapor pressure of 4He.

### 3. Curvature near the critical point

At the critical point, the first derivative of the reduced vapor pressure w.r.t. the reduced temperature takes a fluid-dependent finite value,

$$\frac{dp}{dT_r} \bigg|_{T_{r=1}} = \zeta_c,$$

(16)

usually named Riedel's factor [7]. In general, $\zeta_c$ increases with $\omega$. For example, for the AW equation (10), using equations (12) and (14) one obtains,

$$\zeta_{c,\text{AW}} = - (A_0 + A_1 \omega + A_2 \omega^2),$$

(17)

with $A_0$, $A_1$, and $A_2$ given in table 2. Therefore, for $\omega$ values in the range $-0.4 \leq \omega \leq 1$, typical of the fluids here considered, equation (17) yields $\zeta_c$ values in the range $4 \leq \zeta_c \leq 12$.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$T_c$ (K)</th>
<th>$\omega$</th>
<th>$T_{\text{max}}$</th>
<th>$T_{\text{min}}$</th>
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<td>293.03</td>
<td>0.2566</td>
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<td>0.9845</td>
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<td>0.6721</td>
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<td>0.276</td>
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<td>0.313</td>
<td>0.6773</td>
<td>0.9887</td>
</tr>
<tr>
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<td>0.3052</td>
<td>0.6757</td>
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<td>0.2615</td>
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<td>0.263</td>
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<tr>
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<td>0.9891</td>
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</tr>
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<td>R245fa</td>
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<td>0.6855</td>
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<td>R32</td>
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<td>0.6873</td>
<td>0.991</td>
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<td>R41</td>
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<td>0.6609</td>
<td>0.9868</td>
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<tr>
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<td>0.6824</td>
<td>0.9877</td>
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<td>0.689</td>
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<tr>
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<td>0.9877</td>
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<tr>
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<td>0.6611</td>
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<td>0.2657</td>
<td>0.67</td>
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<td>Xenon</td>
<td>289.73</td>
<td>0.0036</td>
<td>0.6199</td>
<td>0.9866</td>
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The curvature for propane ($\omega = 0.1521$) using equation (1) with the first and second derivatives of the AW equation, given by equations (12) and (13), is also plotted in figure 2(a) by a solid line in the reduced temperature range $0.3 \leq T_r \leq 0.95$. This curvature presents a maximum at $T_{\text{max}} = 0.6507$, very close to the value obtained from NIST data. The reduced temperature of the maximum of the curvature of the AW vapor pressure equation vs. $\omega$ is also plotted in figure 3(a) by a solid line. We can see an excellent agreement between NIST and AW values of $T_{\text{max}}$, except for 4He. Percent relative deviations (102) between NIST and AW data are shown in the inset of figure 3(a). The AARD between NIST and AW data for all fluids is 0.17%. The MARD is obtained for 4He with a value of 4.49%. We ascribe this deviation to the lack of accuracy of the AW equation for the vapor pressure of 4He.

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usually named Riedel's factor [7]. In general, $\zeta_c$ increases with $\omega$. For example, for the AW equation (10), using equations (12) and (14) one obtains,

$$\zeta_{c,\text{AW}} = - (A_0 + A_1 \omega + A_2 \omega^2),$$

(17)

with $A_0$, $A_1$, and $A_2$ given in table 2. Therefore, for $\omega$ values in the range $-0.4 \leq \omega \leq 1$, typical of the fluids here considered, equation (17) yields $\zeta_c$ values in the range $4 \leq \zeta_c \leq 12$.

![Figure 3](image-url)
The CC equation (4) does not satisfy the scaling law (18) and, therefore, using equation (9) its curvature takes a finite value at the critical point given by

$$k_c^{cc} = \frac{A(\omega)}{1 + A(\omega)^2}$$

with $A(\omega)$ given by equation (5). The curvature for propane $(\omega = 0.1521)$ obtained from the CC equation in the range $0.95 < T_r < 1$ is plotted by a dashed line in figure 2(b). One can see that the CC curvature decreases slowly towards the value $k_c^{cc} = 0.1052$ given by equation (20). On the contrary, equations (13) and (15) show that the AW equation satisfies the scaling law (18) with an effective critical exponent $a = 0.5$. Therefore, the curvature of the AW equation also satisfies the scaling law (19) with an exponent $a = 0.5$. The curvature for propane $(\omega = 0.1521)$ obtained from the AW equation in the range $0.95 < T_r < 1$ is plotted by a solid line in figure 2(b). One can see that the AW curvature presents a minimum at a reduced temperature $T_{r,\min} = 0.9886$ and then it quickly increases with $T_r$ so that $k_{AW} \rightarrow \infty$ when $T_r \rightarrow 1$. Since the curvature for both the CC and AW equations has a similar bell-shaped form far enough the critical point, one can conclude that the occurrence of a minimum of the curvature near the critical point can be obtained from vapor pressure equations thermodynamically consistent with the scaling law (18). Therefore, the reduced temperature $T_{r,\min}$ of this minimum can be considered as a marker for the critical region in the sense that it delimits the transition from a regular behavior far the critical point (a bell-shaped form with a maximum) to a singular behavior near the critical point (a divergence prescribed by the renormalization group theory). The curvature for propane using equations (1)–(3) and $\Delta h_p, \rho, \rho_v, c_v^p$, and $c_v^\ell$ data obtained from RefProp 9.0 [3], in the reduced temperature range $0.95 < T_r < 1$ is plotted by symbols in figure 2(b), showing a minimum at $T_{r,\min} = 0.9879$, very close to the above reported value for the minimum of the curvature of the AW equation.

Assuming that the saturated vapor pressure of any real fluid must satisfy the scaling law (18), the curvature of its reduced vapor pressure curve must present a minimum near the critical point. Using equations (1)–(3), we have analyzed the curvature of the 105 substances included in RefProp 9.0 and listed in table 1, in the reduced temperature range $0.95 < T_r < 1$. We find that for most fluids the curvature presents a minimum at a different reduced temperature $T_{r,\min}$ reported in the fourth column of table 1. Figure 3(b) shows a plot of $T_{r,\min}$ vs. $\omega$. Symbols correspond to NIST data using the fourth column of table 1 and the solid line corresponds to the minimum of the curvature of the AW vapor pressure equation, given by equation (9). We can see a fair agreement between NIST and AW values of $T_{r,\min}$. The AARD between NIST and AW data for those fluids is 0.27%. The MARD is obtained for Orthohydrogen with a value of 0.89%. We note the absence of a minimum of the curvature for 25 fluids from NIST data. This absence could be due to the fact that the equation of state used for the NIST program for obtaining vapor pressure data for such fluids might fail near the critical point.

4. Summary

To summarize, we have used the curvature of the reduced vapor pressure curve as an alternative way to analyze the shape of this curve. By using vapor–liquid data of 105 fluids reported in the NIST data base, we find that, far from the critical point, the curvature presents a bell-shaped form with a maximum at a fluid dependent reduced temperature $T_{r,\max}$ belonging to the interval 0.5–0.8 and increasing as the acentric factor $\omega$ increases. On the other hand, near the critical point, the curvature presents a minimum at a fluid dependent reduced temperature $T_{r,\min}$ that belongs to the interval 0.980–0.995. This minimum can only be predicted by considering adequate functional forms for the vapor pressure curve. This happens for vapor pressure equations for which the second derivative w.r.t. the reduced temperature diverges at the critical point. This is the case of the Ambrose–Walton equation, which provides a good agreement between theoretical values for both $T_{r,\max}$ and $T_{r,\min}$ and those obtained from NIST data.

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