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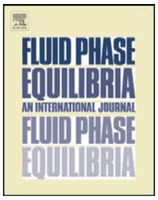

Application of a new crossover treatment to a generalized cubic equation of state

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ABSTRACT

In spite of recent progress in the field of equations of state, the use of cubic equations of state (EoS) such as Redlich–Kwong EoS remains common in the industry. It has already been proved that such classical EoS which follow a mean field approach fail to represent physical properties in the vicinity of the critical point. Moreover, it is well known that in this area the representation of thermodynamic properties must rely on scale invariance. In this work, a new Landau-crossover treatment for pure fluids with two parameters has been applied to a generalized form of cubic EoS. The model calculations have been confronted with experimental data. The crossover treatment allows a correct representation of PVT values in the critical region while keeping classical results at distance. Discussion on possible improvements is also provided.

1. Introduction

In a context of growing concern about environmental issues, supercritical processes are becoming more and more attractive. They are particularly used in the pharmaceutical and food industry where the innocuousness and the physical properties of fluids like supercritical CO_2 are appealing. Besides, supercritical fluids are not only used as extraction solvents but also as chromatography eluents, reaction media, etc.

Up to now, two main different approaches have been used to represent fluids properties in a wide range of PVT values. The first one is the Landau-crossover method. Successfully employed by Sengers and coworkers and also by Kiselev in a simplified way [1], this method consists in rewriting the free energy with the inclusion of a crossover function. This function allows the renormalization of temperature and volume variables as the region of concern gets closer to the critical point. The phenomenological method of Kiselev uses a simple Padé approximant of the crossover free-energy obtained from the numerical solution of the renormalization-group equations. It is supposed to deviate from theoretical solutions [2] but its relative simplicity is fully compatible with chemical engineering issues. However, many authors privileged the second approach: White's recursive procedure [3,4]. The reason claimed is systematically that this model requires a reduced number of parameters [5–9]. In this article, it is therefore our aim to reduce the number of parameters of the Landau-crossover fitted on experimental data. We shall compare the results obtained with those of White's recursive procedure in a next publication.

2. Theory

In the classical Landau theory of critical phenomena [10], it is assumed that the critical part of the free energy, $\Delta\bar{A}$ can be represented by a Taylor expansion in powers of the order parameter φ:

$$\Delta\bar{A} = \sum_{i=0}\sum_{j=1} a_{ij}\tau^i\varphi^j \tag{1}$$

with $\tau = (T/T_c) - 1$, $\varphi = (V/V_c) - 1$ (if the same order parameter as Kiselev is chosen) and a_{ij} system dependent parameters. Therefore, in the critical region,

$$\Delta\bar{A} \approx a_{12}\tau\varphi^2 + a_{04}\varphi^4 \tag{2}$$

since $\varphi \ll 1$ and $\tau \ll 1$.

Chen et al. [11] constructed the following crossover expression for the thermodynamic potential of a system in the critical region:

$$\Delta\bar{A} = a_{12}\tau Y^{(2-\nu^{-1})/\omega} Y^{-\eta/\omega}\varphi^2 + a_{04}\varphi^4 Y^{1/\omega} Y^{-2\eta/\omega} - K(\tau^2) \tag{3}$$

$K(\tau^2)$ is the so-called kernel term which provides the correct scaling behaviour of the isochoric specific heat asymptotically close to the critical point. It will not be used thereafter since derivative properties will not be calculated. The expression (3) is based on the renormalization-group calculations of Nicoll and Albright [12,13] and can be rewritten thanks to scaling laws in the form:

$$\Delta\bar{A} = a_{12}\tau\varphi^2 Y^{(\gamma-2\beta-\alpha)/2\Delta_1} + a_{04}\varphi^4 Y^{(\gamma-2\beta)/\Delta_1} - K(\tau^2) \tag{4}$$

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Table 1
Values of parameters c and d as a function of the EoS.

EoS	Parameter c	Parameter d
Van der Waals [22]	0	0
Redlich–Kwong [19]	0	b
Peng–Robinson [21]	$b(1-\sqrt{2})$	$b(1+\sqrt{2})$
Harmens–Knapp [35]	$\frac{1-c^*}{2}b+\sqrt{\left(\left(\frac{1-c^*}{2}b\right)^2-c^*b^2\right)}$	$\frac{1-c^*}{2}b-\sqrt{\left(\left(\frac{1-c^*}{2}b\right)^2-c^*b^2\right)}$
Patel–Teja [24]	$\frac{b+c^*}{2}+\sqrt{\left(c^*b+\left(\frac{b+c^*}{2}\right)^2\right)}$	$\frac{b+c^*}{2}-\sqrt{\left(c^*b+\left(\frac{b+c^*}{2}\right)^2\right)}$

In all these equations η, ω, γ, β, α, ν and Δ_1 are critical exponents.

The values from [14] have been used for the calculations:

$$\alpha = 0.110,\ \beta = 0.325,\ \gamma = 1.239 \text{ and } \Delta_1 = 0.51$$

Y is the crossover function and depends on the distance to the critical point.

It is then easy to verify that, following the proposition of Kiselev, the renormalization of the variables τ and φ into (Eq. (5)) allows the crossover from (4) to (2) to be asymptotically verified.

$$\bar{\tau} = \tau Y^{-(\alpha/2\Delta_1)} \text{ and } \bar{\varphi} = \varphi Y^{(\gamma-2\beta)/2\Delta_1} \tag{5}$$

Starting from a Wegner expansion [15], Kiselev et al. represented the Helmholtz free energy in a parametric form (6) [16] which is physically equivalent to the six-term crossover model [2,17].

$$\begin{aligned}
\Delta\bar{A}(r,\theta) &= kr^{2-\alpha}R^{\alpha}(q)\left[a\Psi_0(\theta)+\sum_{i=1}^{5}c_i r^{\Delta_i}R^{-\Delta_i}(q)\Psi_i(\theta)\right]\\
\tau &= r(1-b^2\theta^2)\\
\varphi &= kr^{\beta}R^{-\beta+1/2}(q)\theta + d_1\tau
\end{aligned} \tag{6}$$

q is related to the parametric variable r by:

$$q^2 = rg = \frac{r}{G} \tag{7}$$

It has been proved that g is proportional to the inverse of the Ginzburg number which evaluates the size of the fluctuation zone. The crossover function $R(q)$ was introduced in order to suppress the singularities in the expansion (6) when q tends to infinity.

It is possible to show (see [18]) that (6) can be written in the form of (4). Then, considering the link between Y and $R(q)$:

$$Y(q) = \left(\frac{q^2}{R(q)}\right)^{\Delta_1} \tag{8}$$

We take here into account the so-called root-square corrections for the isochoric specific heat and because of the limits:

$$R(q)\overset{q\to\infty}{\longrightarrow}q^2 \text{ and } R(q)\overset{q\to 0}{\longrightarrow}1 \tag{9}$$

$$Y(q)\overset{q\to\infty}{\longrightarrow}1 \text{ and } Y(q)\overset{q\to 0}{\longrightarrow}q^{2\Delta_1} \tag{10}$$

this crossover function allows to switch progressively from Chen et al. expression (4) close to the critical point to the Landau expression (2) as q increases.

3. Classical equation of state

The Landau-crossover has been applied to a cubic equation of state. Classical equations of state, like RKS [19,20] and Peng–Robinson [21], are mainly used in chemical engineering to represent the behaviour of pure component and mixtures. They belong to Van der Waals equation's [22] family which is equivalent to a (mean field) Landau theory next to the critical point. Moreover, they require only the knowledge of critical properties (T_c and P_c). Process optimization needs accurate thermodynamics models which can predict densities and phase equilibria in a large range of temperatures. The classical equations of state have been modified several times during the last 30 years particularly in order to improve the densities determination around the critical point. Peneloux et al. [23] enhanced the representation of liquid densities thanks to a volume translation but failed to represent the densities close to the critical point. Patel and Teja [24] introduced a third parameter (dependent on critical compressibility) and modified the attractive part of classical EoS. They improved the representation of the densities but not satisfactory enough in the critical region.

In this work, the critical part $\Delta\bar{A}$ has been extracted from a generalized equation of state following Zielke and Lempe [25] concept. Their generalization presents the advantage to provide a single form for the calculation of physical properties which is valid for every cubic EoS. Indeed, a classical cubic EoS can be written as:

$$P = \frac{RT}{v-b} - \frac{a(T)}{(v+c)(v+d)} \tag{11}$$

where P is the pressure, v is the molar volume, R is the gas constant and T is the temperature. As shown in Table 1, the two parameters c and d can be expressed from the parameters b and c^* of the original form of the cubic EoS. $a(T)$ depends on the choice of the alpha function but also on T_c and P_c values as it is explained in Ji and Lempe paper [26]. The determination of the critical parameters Ω_a, Ω_b and Ω_{c^*} which are linked to a, b and c^* in Eq. (12) is done by solving Eq. (11) developed in volume at the critical point.

$$\begin{aligned}
a(T) &= \Omega_a\frac{RT_c^2}{P_c^2}\alpha(T)\\
b &= \Omega_b\frac{RT_c}{P_c}\\
c^* &= \Omega_c\frac{RT_c}{P_c}
\end{aligned} \tag{12}$$

In this paper, we have selected the RKS EoS because it is one of the mostly used equations in the industry and this equation fails strongly in the representation of densities. In a near future, we will also compare our results with the ones obtained following White's procedure applied to RKS EoS [5]. Finally, $c=0$ and $b=d$.

An important remark must be made for programming purpose. If RKS (or PR) EoS is selected, Z_c is supposed to be constant for any fluid. However, our experience proved that if Ω_a and Ω_b are not expressed with enough digits, the critical compressibility is not the one expected. This implies deviations in the calculation of the critical shift described below. As a consequence, we recommend to use (Eq. (13)) instead of their evaluation as in the original publication [19].

$$\begin{aligned}
\Omega_a &= \frac{1}{9(2^{1/3}-1)}\\
\Omega_b &= \frac{2^{1/3}-1}{3}
\end{aligned} \tag{13}$$