

## The Soave, Twu and Boston–Mathias alpha functions in cubic equations of state Part I. Theoretical analysis of their variations according to temperature

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### ABSTRACT

A theoretical analysis of the strengths and weaknesses of the Soave, Twu and Boston–Mathias attractive terms was performed with the Redlich–Kwong EoS. Special attention was paid to the variations of the alpha functions and their first and second derivatives with respect to temperature. Contrary to the Soave function, abnormal behaviors of the derived Twu and Boston–Mathias functions were evidenced in the temperature range commonly covered by industrial applications. The unsuccessful variations of the derived alpha functions observed with these two last models strengthen the interest of the Soave equation for the modeling of derived thermodynamic properties. The accuracy of pure component data modeling by means of the cubic equation of state is discussed in a second part.

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### 1. Introduction

Cubic equations of state (EoS) are widely used in industrial applications for their simplicity and accuracy in predicting pure compound and mixture thermodynamic properties in vapor and liquid phases. The ability of these equations in correlating phase equilibria of mixtures depends, not only on the choice of appropriate mixing rules, but also on the attractive term selected for the pure components.

A remarkable step forward in the practical application of cubic EoS was performed by Soave's work [1]. Thanks to his generalized formulation of the alpha function  $\alpha(T_r)$  with respect to the acentric factor, it was possible to adequately correlate the vapor pressures of non-polar or slightly polar compounds at high reduced temperatures. However, beside the fact that the Soave function is assumed to provide less satisfactory predictions at low reduced temperatures and for polar compounds, its major limitation comes from its abnormal extrema at the supercritical region; with this formulation, the attractive term does not decrease monotonically with increasing temperatures. To overcome this problem, several authors (Mathias [2], Mathias and Copeman [3], Stryjek and Vera [4]) tried to improve the Soave alpha function by adding extra terms; however, these modifications, not only keep the inherent weakness of the original

approach, but usually introduce not suitable deviations in the prediction of derived thermodynamic properties, such as enthalpies or heat capacities.

A second important step in the calculation of vapor pressures by means of cubic EoS was performed by Twu and coworkers [5] with a new alpha function inspired from the works of Boston and Mathias [6], Trebble and Bishnoi [7] and Melhem et al. [8], and which exhibits a satisfactory variation with increasing temperatures. In the original work, the characteristic  $\alpha(T_r)$  parameters were determined for individual components; a generalized version, depending only on the knowledge of the acentric factor, was proposed later by the authors [9,10] for the Peng–Robinson [11] and the Redlich–Kwong [12] equations of state. This model is now used in routine in current simulators and is also introduced in the VTPR group contribution method developed by Ahlers and Gmehling [13,14].

Most of the works concerned with the comparison of literature attractive terms [15,16] only focuses on the representation of pure component saturation properties, mainly vapor pressures. However, if this approach is justified by the fact the alpha function parameters are usually tuned on saturation data, it does not allow separating the influence of the alpha function with respect to temperature from that of the equation of state with respect to pressure. In addition, even in works concerned with multiproperty analysis [17,18] or the pitfalls of the Soave type function for the estimation of the Joule–Thomson coefficient [19], the analysis of the first and second derivatives of the alpha functions, which occur

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in the calculation of enthalpies and heat capacities, are completely neglected.

In this work, devoted to pure compounds, we reconsider attractive terms widely used in industrial applications and studied in literature [15,16], namely the Soave [1], Boston–Mathias [6] and Twu [5,9,10] functions. For simplicity, the Redlich–Kwong equation was only considered, but the conclusions drawn from this study can easily be extended to the Peng–Robinson equation. The Part I is concerned with the theoretical analysis of the  $\alpha(T_r)$  functions according to temperature; for this purpose, the variations of the alpha functions and their first and second derivatives were studied in the temperature range usually covered by industrial applications. The Part II [20] deals with the modeling of saturation data and liquid enthalpies and heat capacities under pressure; in that part, an analysis of the influence of the attractive terms with respect to temperature and pressure is performed for individual compounds, including hydrocarbons and polar substances.

## 2. Literature alpha functions and their derivatives

Two types of alpha functions were considered: the generalized models, Soave, Twu et al. and Boston–Mathias depending only on the knowledge of the acentric factor  $\omega$ , and the Twu et al. function which requires individual component parameters. The alpha functions associated with the Redlich–Kwong EoS are given by the following expressions:

(a) The generalized “Soave( $\omega$ )” function proposed by Soave [1]:

$$\alpha = [1 + m(1 - \sqrt{T_r})]^2 \quad (1)$$

in which, the parameter  $m$  is correlated to the acentric factor  $\omega$  through the generalized expression:

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \quad (2)$$

The values of  $m$  corresponding respectively to acentric factors  $\omega$  equal to zero and to unit are given in Table 1.

(b) The “Twu(LMN)” equation originally developed by Twu et al. [5] in order to improve the correlation of vapor pressures:

$$\alpha = T_r^\delta \exp[L(1 - T_r^\gamma)], \quad \delta = N(M - 1), \quad \gamma = NM \quad (3)$$

and for which, the  $L$ ,  $M$  and  $N$  parameters are determined for individual components. The values published by the authors [10,21] for the hydrocarbons and polar compounds considered in this work are reported in Table 2; the values of  $T_c$  and  $\omega$  listed in this table were taken from Reid. et al. [22].

**Table 1**  
The generalized Twu ( $\omega$ ) and Boston–Mathias( $\omega$ ) parameters for subcritical and supercritical conditions.

Alpha parameters	$T_r \leq 1$		$T_r > 1$	
	$\alpha_{\text{sub}}^{(0)}$	$\alpha_{\text{sub}}^{(1)}$	$\alpha_{\text{sup}}^{(0)}$	$\alpha_{\text{sup}}^{(1)}$
Twu				
$L$	0.141599	0.500315	0.441411	0.032580
$M$	0.919422	0.799457	6.500018	1.289098
$N$	2.496441	3.291790	−0.200000	−8.000000
Boston–Mathias				
$m$	0.480000	1.878000	–	–
$c$	–	–	0.3870968	0.968540
$d$	–	–	1.2400000	1.939000

**Table 2**

Pure component parameters together with the  $L$ ,  $M$ ,  $N$  parameters used with the Twu(LMN) function for individual compounds.

Components	$T_c$ (K)	$\omega$	$L$	$M$	$N$	References
Methane	190.40	0.011	0.106750	0.920161	3.09674	[10]
Pentane	469.70	0.251	0.305259	0.835681	2.08969	[10]
Pentane	469.70	0.251	0.379229	0.841706	1.82331	[21]
Hexane	507.50	0.299	0.128223	0.893666	4.88241	[10]
Hexane	507.50	0.299	0.158080	0.872819	3.84418	[21]
Heptane	540.30	0.349	0.206521	0.852664	3.32097	[10]
Heptane	540.30	0.349	0.340339	0.844963	2.38332	[21]
Decane	617.70	0.489	0.316547	0.828468	2.90395	[10]
Eicosane	767.00	0.907	1.949590	1.180080	0.78281	[10]
Cyclohexane	553.50	0.212	0.151079	0.865944	3.17613	[10]
Cyclohexane	553.50	0.212	0.245880	0.845046	2.25895	[21]
Benzene	562.20	0.212	0.106109	0.890646	4.31730	[10]
Benzene	562.20	0.212	0.163664	0.860016	2.98498	[21]
Acetone	508.10	0.304	0.479844	0.870627	1.79010	[21]
Methanol	512.60	0.556	0.690551	0.911298	1.96941	[21]
Ethanol	513.90	0.644	1.076460	0.964661	1.35369	[21]
Water	647.30	0.344	0.413297	0.874988	2.19435	[21]

(c) The generalized “Twu( $\omega$ )” equation proposed later by Twu et al. [10] as a predictive version with respect to the acentric factor:

$$\alpha = \alpha^{(0)} + \omega(\alpha^{(1)} - \alpha^{(0)}) \quad (4)$$

the  $\alpha^{(0)}$  and  $\alpha^{(1)}$  functions show the same dependence on the reduced temperature as the  $\alpha$  function (Eq. (3)) except that each of them makes use of generalized sets of  $L$ ,  $M$  and  $N$  parameters; in addition, for each  $\alpha^{(0)}$  and  $\alpha^{(1)}$  function, two sets of parameters are recommended for subcritical and supercritical conditions. The corresponding values are given in Table 1.

(d) The generalized “Boston–Mathias( $\omega$ )” equation proposed by the authors [6] as a mixed version of alpha terms:

For  $T_r \leq 1$ :  $\alpha(T_r)$  is given by the Soave( $\omega$ ) function (Eqs. (1) and (2))

$$\text{For } T_r > 1: \alpha(T_r) = \exp[c(1 - T_r^d)] \quad (5)$$

Parameters  $c$  and  $d$  are correlated to the  $m$  parameter (Eq. (2)) through the general expressions:

$$d = 1 + \left(\frac{m}{2}\right), \quad c = \frac{m}{d} \quad (6)$$

The values of  $c$  and  $d$  corresponding respectively to acentric factors  $\omega$  equal to zero and to unit are also given in Table 1.

The Soave, Twu and Boston–Mathias alpha functions, together with their first and second derivatives, are detailed in Table 3. In order to make easier their analysis according to temperature, the following  $h_\alpha$  and  $C_\alpha$  functions, occurring respectively in the expressions of the enthalpy and the heat capacity, were defined:

$$h_\alpha = \frac{d(\alpha/T_r)}{d(1/T_r)} = \alpha - T_r \frac{d\alpha}{dT_r}, \quad C_\alpha = \frac{dh_\alpha}{dT_r} = -T_r \frac{d^2\alpha}{dT_r^2} \quad (7)$$

For each model, the variations of  $\alpha$ ,  $h_\alpha$  and  $C_\alpha$  were studied in a wide range of reduced temperatures and special attention was paid to the location of possible singular points. In particular, we focus on:

(I) *Extrema of the alpha function*; the corresponding reduced temperatures are obtained as:

$$T_{r(\alpha, \text{extrem})} \quad \text{for} \quad \left(\frac{d\alpha}{dT_r}\right) = 0 \quad (8)$$

with the first derivatives (Eqs. (A1), (A2) and (A3)) given in Table 3 for the various models.

**Table 3**

The Soave, Twu and Boston–Mathias alpha functions together with their derivatives with respect to temperature.

<b>Soave</b>	
$\alpha(T_r) = [1 + m(1 - \sqrt{T_r})]^2$	$\frac{d\alpha}{dT_r} = -\frac{m}{\sqrt{T_r}}[1 + m(1 - \sqrt{T_r})]$ (A1)
$h_\alpha = \alpha - T_r \frac{d\alpha}{dT_r} = \alpha + m\sqrt{T_r}[1 + m(1 - \sqrt{T_r})]$	$\frac{d^2\alpha}{dT_r^2} = \frac{m}{2T_r^{3/2}}(1 + m)$ (B1)
$C_\alpha = -T_r \frac{d^2\alpha}{dT_r^2} = -\frac{m}{2\sqrt{T_r}}(1 + m)$	$\frac{d^2h_\alpha}{dT_r^2} = \frac{m(1 + m)}{4T_r^{3/2}}$ (C1)
<b>Twu</b>	
$\alpha(T_r) = T_r^\delta \exp[L(1 - T_r^\gamma)]$	$\frac{d\alpha}{dT_r} = \alpha T_r^{-1}(\delta - X)$ (A2)
with: $\delta = N(M - 1)$ , $\gamma = NM$	with: $X = L\gamma T_r^\gamma$
$h_\alpha = \alpha - T_r \frac{d\alpha}{dT_r} = \alpha(1 - \delta + X)$	$\frac{d^2\alpha}{dT_r^2} = \alpha T_r^{-2}(X^2 + BX + C)$ (B2)
$C_\alpha = -T_r \frac{d^2\alpha}{dT_r^2} = -\alpha T_r^{-1}(X^2 + BX + C)$	with: $B = 1 - 2\delta - \gamma$ , $C = \delta(\delta - 1)$
	$\frac{d^2h_\alpha}{dT_r^2} = \alpha T_r^{-2}(X^3 + DX^2 + EX + F)$ (C2)
	with: $\begin{cases} D = 2 - 3\delta - 3\gamma \\ E = C + B(1 - \delta - \gamma) \\ F = C(1 - \delta) \end{cases}$
<b>Boston–Mathias</b>	
$\alpha(T_r) = \exp[c(1 - T_r^d)]$	$\frac{d\alpha}{dT_r} = -\alpha T_r^{-1}X$ (A3)
	with: $X = cdT_r^d$
$h_\alpha = \alpha - T_r \frac{d\alpha}{dT_r} = \alpha(1 + X)$	$\frac{d^2\alpha}{dT_r^2} = \alpha T_r^{-2}X(X - d + 1)$ (B3)
$C_\alpha = -T_r \frac{d^2\alpha}{dT_r^2} = \alpha T_r^{-1}X(d - X - 1)$	$\frac{d^2h_\alpha}{dT_r^2} = \alpha T_r^{-2}X(X^2 + BX + C)$ (C3)
	with: $B = 2 - 3d$ , $C = (d - 1)^2$

(II) Inflexion points of the alpha function, leading to a zero value of  $C_\alpha$ ; they involve the following conditions:

$$T_{r(\alpha, \text{inflex})} = T_{r(C_\alpha=0)} \quad \text{for} \quad C_\alpha = -T_r \left( \frac{d^2\alpha}{dT_r^2} \right) = 0 \quad (9)$$

where the expressions of the second derivatives are given in Table 3 (Eqs. (B1), (B2) and (B3)).

(III) Inflexion points of the  $h_\alpha$  function, leading to extrema of  $C_\alpha$ ; the corresponding reduced temperatures are given by:

$$T_{r(h_\alpha, \text{inflex})} = T_{r(C_\alpha, \text{extrem})} \quad \text{for} \quad \left( \frac{d^2h_\alpha}{dT_r^2} \right) = \left( \frac{dC_\alpha}{dT_r} \right) = 0 \quad (10)$$

with the third derivatives ( $d^3\alpha/dT_r^3$ ) reported in Table 3 (Eqs. (C1), (C2) and (C3)).

The values of singular temperatures obtained for the various models investigated in this work are reported in Table 4.

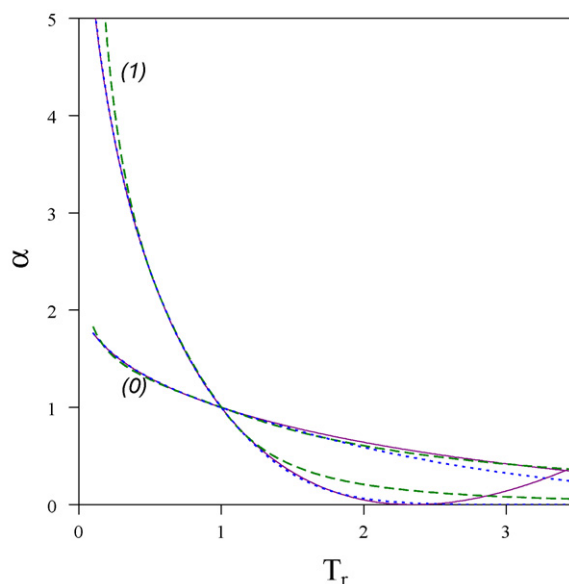
### 3. Results and discussion

The first part of this section is devoted to the analysis of the generalized Soave( $\omega$ ), Twu( $\omega$ ) and Boston–Mathias( $\omega$ ) functions; results obtained are thus completely independent on the properties and polarity of pure compounds. In the second part, the Twu(LMN) function is considered for some representative hydrocarbons and polar compounds.

#### 3.1. Behavior of the generalized Soave, Twu and Boston–Mathias models

The comparison between the different alpha terms is based on the analysis of the  $\alpha^{(0)}$  and  $\alpha^{(1)}$  functions, as defined with the

Twu( $\omega$ ) model (Eq. (4)). These functions are representative of specific compounds having respectively acentric factors  $\omega$  equal to zero and to unity, but nevertheless they allow estimating the behavior of a great number of organic compounds with intermediate acentric factors. Figs. 1, 3 and 4 illustrate the variations of the corresponding  $\alpha$ ,  $h_\alpha$  and  $C_\alpha$  functions with respect to the reduced temperature  $T_r$ .



**Fig. 1.** Variations of the generalized  $\alpha$  functions with respect to the reduced temperature for:  $^{(0)}\omega = 0$  and  $^{(1)}\omega = 1$ ; models: (—) Soave( $\omega$ ); (---) Twu( $\omega$ ) and (....) Boston–Mathias( $\omega$ ).

**Table 4**Singular point temperatures observed for the  $\alpha$ ,  $h_\alpha$  and  $C_\alpha$  curves calculated for various sets of parameters.

Parameters from the generalized functions (Table 1)							
$\alpha$ type function	$T_{r(\alpha, \text{extrem})}$	$T_{r(\alpha, \text{inflex})} = T_{r(C_\alpha = 0)}$		$T_{r(h_\alpha, \text{inflex})} = T_{r(C_\alpha, \text{extrem})}$			
Soave ( $\alpha^{(0)}$ )	9.507	–	–	–	–	–	–
Soave ( $\alpha^{(1)}$ )	2.348	–	–	–	–	–	–
Twu ( $\alpha_{\text{sub}}^{(0)}$ )	–	–	–	1.185 <sup>*</sup>	2.971 <sup>*</sup>	–	–
Twu ( $\alpha_{\text{sup}}^{(0)}$ )	0.606 <sup>*</sup>	0.229 <sup>*</sup>	0.978 <sup>*</sup>	0.152 <sup>*</sup>	0.356 <sup>*</sup>	1.529	–
Twu ( $\alpha_{\text{sub}}^{(1)}$ )	–	–	–	0.930	1.423 <sup>*</sup>	–	–
Twu ( $\alpha_{\text{sup}}^{(1)}$ )	0.829 <sup>*</sup>	0.690 <sup>*</sup>	0.963 <sup>*</sup>	0.641 <sup>*</sup>	0.749 <sup>*</sup>	1.109	–
Boston–Mathias ( $\alpha_{\text{sup}}^{(0)}$ )	–	0.572 <sup>*</sup>	–	0.071 <sup>*</sup>	2.754	–	–
Boston–Mathias ( $\alpha_{\text{sup}}^{(1)}$ )	–	0.699 <sup>*</sup>	–	0.351 <sup>*</sup>	1.393	–	–
Twu $L$ , $M$ and $N$ parameters for individual compounds (Table 2)							
Compounds	References	$T_{r(\alpha, \text{extrem})}$	$T_{r(\alpha, \text{inflex})} = T_{r(C_\alpha = 0)}$		$T_{r(h_\alpha, \text{inflex})} = T_{r(C_\alpha, \text{extrem})}$		
Methane	[10]	–	0.983	1.553	1.269	2.731	–
Pentane	[10]	–	–	–	1.347	1.953	–
Pentane	[21]	–	–	–	–	–	–
Hexane	[10]	–	0.932	1.325	1.144	1.874	–
Hexane	[21]	–	–	–	1.131	2.063	–
Heptane	[10]	–	–	–	0.399	2.737	–
Heptane	[21]	–	–	–	1.038	1.924	–
Decane	[10]	–	–	–	1.045	1.834	–
Eicosane	[10]	0.063	0.231	–	0.722	–	–
Cyclohexane	[10]	–	–	–	1.214	2.385	–
Cyclohexane	[21]	–	–	–	1.276	2.299	–
Benzene	[10]	–	1.051	1.380	1.221	2.125	–
Benzene	[21]	–	–	–	1.221	2.415	–
Acetone	[21]	–	–	–	0.909	1.670	–
Methanol	[21]	–	–	–	0.554	1.525	–
Ethanol	[21]	–	–	–	0.242	1.154	–
Water	[21]	–	–	–	0.847	1.874	–

\* Singular points observed for temperatures outside of the range of use.

### 3.1.1. The Soave( $\omega$ ) model

As shown in Fig. 1, the  $\alpha^{(0)}$  and  $\alpha^{(1)}$  functions exhibit the expected extrema at supercritical conditions for the reduced temperatures given by (Eqs. (8), (A1)):

$$T_{r(\alpha, \text{extrem})} = \frac{T_{(\alpha, \text{extrem})}}{T_c} = \left(1 + \frac{1}{m}\right)^2 \quad (11)$$

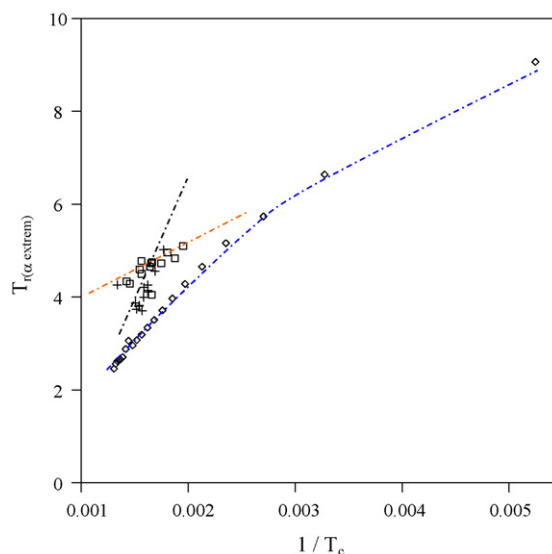
The values obtained for  $m^{(0)}$  and  $m^{(1)}$  are reported in Table 4. Fig. 2 illustrates the variations of  $T_{r(\alpha, \text{extrem})}$  with respect to the inverse of the critical temperature for a series of hydrocarbons:  $n$ -alkanes (from methane to eicosane), cycloalkanes (from cyclopentane to cyclooctane) and aromatics (from benzene to naphthalene). For all these families, a quasi linear dependence was observed, leading to minima located around  $T_{(\alpha, \text{extrem})} = 1800$  K for  $n$ -alkanes, 1300 K for cycloalkanes and 2100 K for aromatics. For the polar compounds considered in the next section, the same order of magnitude was found, with  $T_{(\alpha, \text{extrem})}$  about 1500–2600 K. In addition, even if this work is mainly concerned with the Redlich–Kwong equation, it should be noted that the same results were obtained with the Peng–Robinson EoS [11], except that the minima were located at even higher temperatures, approximately one and a half times those obtained with the Redlich–Kwong equation. Thus, whatever the cubic EoS, the temperature range of the abnormal behavior of the Soave equation is far beyond the domain of current industrial applications.

The behavior of the first and second derivatives  $h_\alpha^{(0)}$  and  $h_\alpha^{(1)}$ , on one hand, and  $C_\alpha^{(0)}$  and  $C_\alpha^{(1)}$ , on the other hand, is illustrated in Figs. 3 and 4. It can be observed that, for both functions, the Soave model provides a consistent monotonous variation with respect to temperature. The analysis of the singular points reported in Table 4

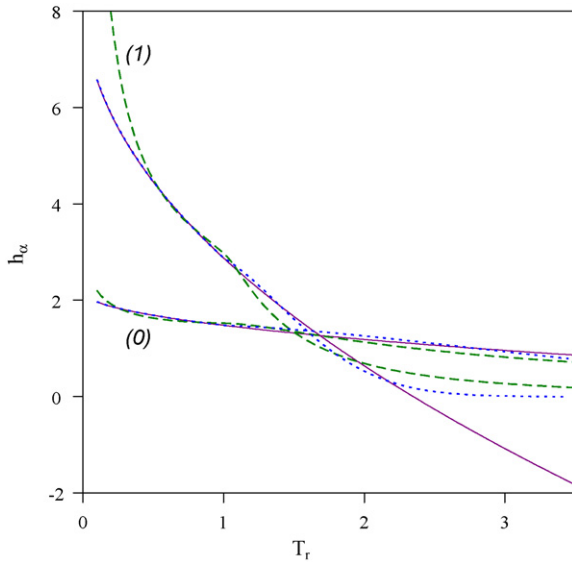
confirms that the  $\alpha$  and  $h_\alpha$  functions present no inflexion points, so that the  $C_\alpha$  functions are always negative and monotonically increase with increasing temperatures.

### 3.1.2. The Twu( $\omega$ ) model

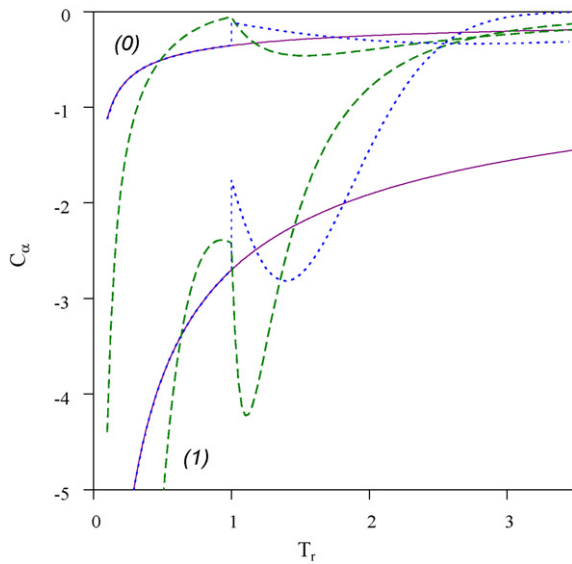
As expected, whatever the temperature range considered, the  $\alpha^{(0)}$  and  $\alpha^{(1)}$  Twu functions (Fig. 1) have a consistent monotonous



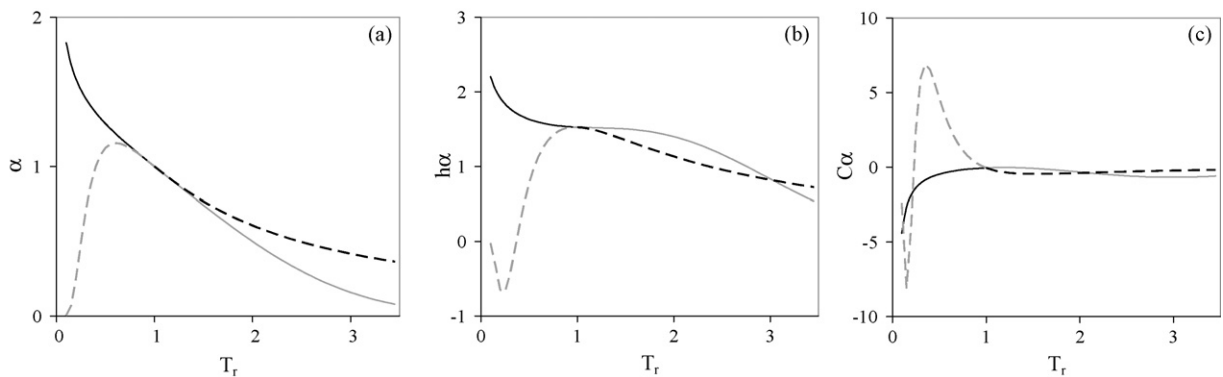
**Fig. 2.** Variation of the reduced temperature  $T_{r(\alpha, \text{extrem})}$  of the minima of the Soave function with respect to  $1/T_c$ : ( $\diamond$ )  $n$ -alkanes; ( $\square$ ) cycloalkanes; (+) aromatics.



**Fig. 3.** Variations of the generalized  $h_\alpha$  functions with respect to the reduced temperature for:  $(0)\omega = 0$  and  $(1)\omega = 1$ ; models: (—) Soave( $\omega$ ) (---) Twu( $\omega$ ) and (....) Boston–Mathias( $\omega$ ).



**Fig. 4.** Variations of the generalized  $C_\alpha$  functions with respect to the reduced temperature for:  $(0)\omega = 0$  and  $(1)\omega = 1$ ; models: (—) Soave( $\omega$ ) (---) Twu( $\omega$ ) and (....) Boston–Mathias( $\omega$ ).



**Fig. 5.** Variations of the alpha terms (a)  $\alpha_{\text{sub}}^{(0)}$ ,  $\alpha_{\text{sup}}^{(0)}$  and their derivatives (b)  $h_{\alpha_{\text{sub}}}^{(0)}$ ,  $h_{\alpha_{\text{sup}}}^{(0)}$  and (c)  $C_{\alpha_{\text{sub}}}^{(0)}$ ,  $C_{\alpha_{\text{sup}}}^{(0)}$  for the Twu( $\omega$ ) model using: (—) subcritical and (---) supercritical parameters; bold patterns refer to the curves in their range of use.

decrease with increasing temperatures, without any discontinuity at the critical point; we can also notice that, for subcritical conditions, the Twu calculations are quite close to the Soave ones. Concerning the first and second derivatives, the  $h_{\alpha}^{(0)}$ ,  $h_{\alpha}^{(1)}$  (Fig. 3) and  $C_{\alpha}^{(0)}$ ,  $C_{\alpha}^{(1)}$  curves (Fig. 4) exhibit singular points for reduced temperatures between 0.5 and 1.5. In order to understand the reasons of these abnormal behaviors, the following analysis was performed:

- for each attractive term  $\alpha^{(0)}$  and  $\alpha^{(1)}$ , we consider, in the whole range of temperatures, the variations of the  $\alpha_{\text{sub}}^{(0)}$ ,  $\alpha_{\text{sup}}^{(0)}$  and  $\alpha_{\text{sub}}^{(1)}$ ,  $\alpha_{\text{sup}}^{(1)}$  functions obtained by using the Twu(LMN) model (Eq. (3)) with the subcritical and supercritical  $L$ ,  $M$  and  $N$  parameters given in Table 1. The behavior of the  $\alpha_{\text{sub}}^{(0)}$ ,  $\alpha_{\text{sup}}^{(0)}$  functions and their derivatives is illustrated in Fig. 5.
- The location of possible extrema or inflexion points in the corresponding functions was determined and the positive values of the singular temperatures are reported in Table 4.

According to (Eqs. (8), (A2)), the extrema of the  $\alpha$  function were estimated from:

$$T_{r(\alpha, \text{extrem})} = \left[ \frac{\delta}{(LY)} \right]^{1/\gamma} \quad (12)$$

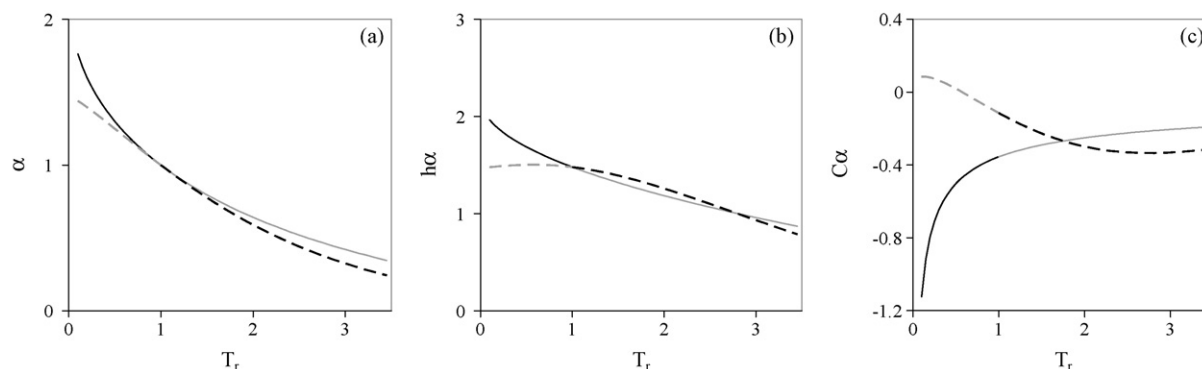
As shown in Table 4, extrema were found only for the supercritical  $\alpha_{\text{sup}}^{(0)}$  and  $\alpha_{\text{sup}}^{(1)}$  functions; however, they are located at temperatures out of the range of their use (respectively, 0.606 and 0.829).

The calculation of the inflexion points of the  $\alpha$  and  $h_\alpha$  functions was performed according respectively to (Eqs. (9), (B2)) and (Eqs. (10), (C2)). Table 4 also shows that only the  $\alpha_{\text{sup}}^{(0)}$  and  $\alpha_{\text{sup}}^{(1)}$  functions present two inflexion points, located outside of the range of use; however, all the  $h_{\alpha_{\text{sub}}}^{(0)}$ ,  $h_{\alpha_{\text{sup}}}^{(0)}$  and  $h_{\alpha_{\text{sub}}}^{(1)}$ ,  $h_{\alpha_{\text{sup}}}^{(1)}$  functions present, at least, two inflexion points which, in most cases, occur in the range of use. Fig. 5a and b illustrate the behavior of  $\alpha^{(0)}$  and  $h_{\alpha}^{(0)}$ . As a consequence, the corresponding  $C_{\alpha}^{(0)}$  curves (Fig. 5c) exhibit abnormal extrema in this temperature range. The existence of these singularities is due to the complexity of the Twu model (Eq. (3)) with respect to the  $L$ ,  $M$  and  $N$  parameters.

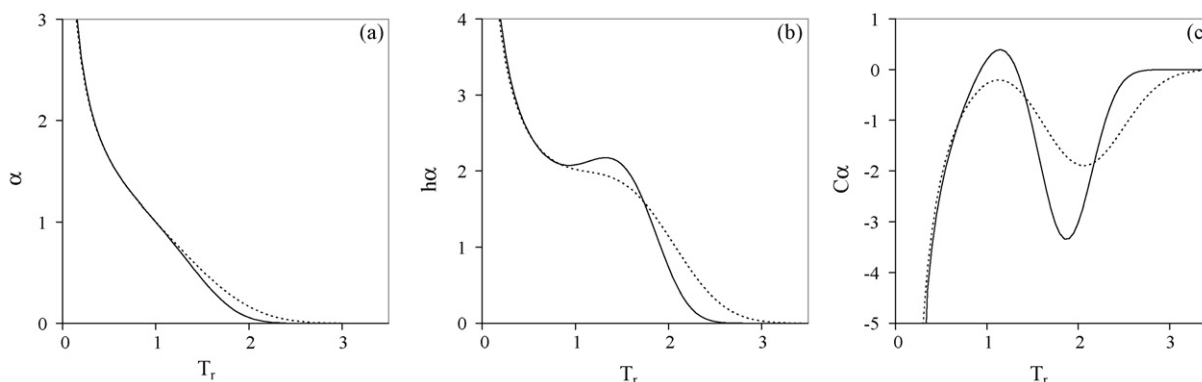
Finally, even if the use of two different sets of  $L$ ,  $M$  and  $N$  parameters introduces break points in the first and second derivatives  $h_\alpha$  and  $C_\alpha$ , it ensures a continuous variation at the critical point.

### 3.1.3. The Boston–Mathias ( $\omega$ ) model

The attractive  $\alpha$  term and its derivatives are presented in Figs. 1, 3 and 4. For supercritical conditions, the functions present



**Fig. 6.** Variations of the alpha terms (a)  $\alpha_{\text{sub}}^{(0)}$ ,  $\alpha_{\text{sup}}^{(0)}$  and their derivatives (b)  $h_{\alpha,\text{sub}}^{(0)}$ ,  $h_{\alpha,\text{sup}}^{(0)}$  and (c)  $C_{\alpha,\text{sub}}^{(0)}$ ,  $C_{\alpha,\text{sup}}^{(0)}$  for the Boston–Mathias( $\omega$ ) model using: (—) subcritical and (---) supercritical parameters; bold patterns refer to the curves in their range of use.

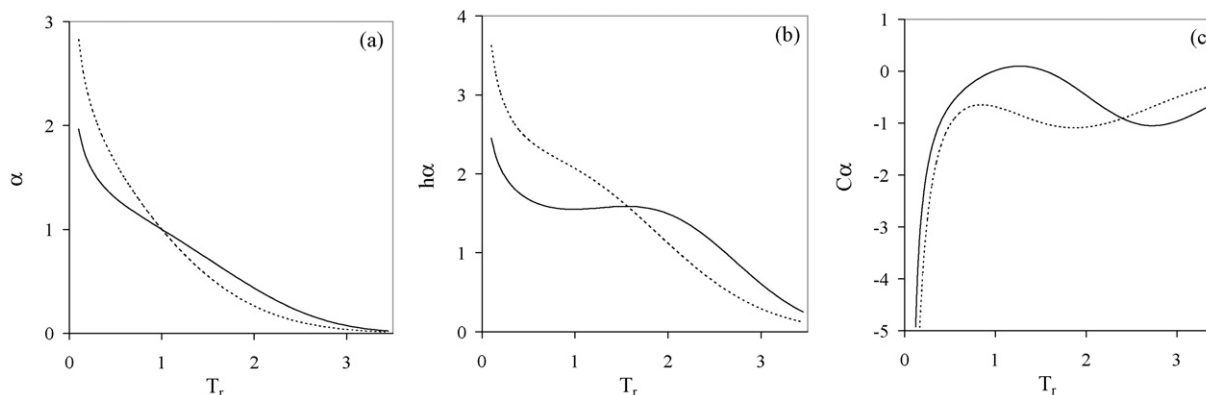


**Fig. 7.** Variations of the alpha term (a)  $\alpha$  and its derivatives (b)  $h_{\alpha}$  and (c)  $C_{\alpha}$  for hexane using the original Twu(LMN) model with the individual parameters from Table 2: (—) Twu et al. [10]; (---) Twu et al. [21].

abnormal singularities similar to those observed with the Twu model. As in the previous case:

- The  $\alpha_{\text{sub}}^{(0)} = \alpha_{\text{soave}}^{(0)}$  and  $\alpha_{\text{sup}}^{(0)}$  functions obtained by using respectively, the Soave( $\omega$ ) model (Eq. (1)) and the Boston–Mathias( $\omega$ ) equation (Eq. (5)) with parameters given in Table 1, were plotted in Fig. 6 in the whole temperature range.
- The location of possible extrema or inflexion points was determined (Table 4) according to (Eqs. (8)–(10)) associated with the derivatives (Eqs. (A3)–(C3)) given in Table 3.

It can be observed (Table 4) that, the  $\alpha_{\text{sup}}^{(0)}$  and  $\alpha_{\text{sup}}^{(1)}$  functions present no extrema, but two inflexion points, however located outside of the range of use ( $T_r = 0.572$  and  $0.699$ ). As for the Twu model, each  $h_{\alpha,\text{sub}}^{(0)}$  and  $h_{\alpha,\text{sup}}^{(1)}$  function presents one inflexion point located in the range of use. As a consequence, the corresponding  $C_{\alpha,\text{sub}}^{(0)}$  and  $C_{\alpha,\text{sup}}^{(1)}$  curves exhibit abnormal extrema in this temperature range. Contrary to the Twu model, the change of  $\alpha$  function at critical conditions, not only introduces break points in the first and second derivatives, but leads to a strong discontinuity in the  $C_{\alpha}$  function at the critical point.



**Fig. 8.** Variations of the alpha term (a)  $\alpha$  and its derivatives (b)  $h_{\alpha}$  and (c)  $C_{\alpha}$  using the original Twu(LMN) model with the individual parameters from Table 2: (—) methane [10]; (---) water [21].



### 3.2. Behavior of the Twu model with individual $L$ , $M$ and $N$ parameters

In this section, the  $Twu(LMN)$  function (Eq. (3)) is considered for some representative hydrocarbons and polar compounds. The list of components considered is given in Table 2 together with the  $L$ ,  $M$  and  $N$  parameters published by the authors [10,21]. For some compounds two sets of parameters were available, which allowed to check the influence of the parameter estimation on the behavior of the attractive terms. Hydrocarbons and polar compounds were chosen in order to represent a wide range of acentric factor.

The typical curves obtained for hexane with two sets of  $L$ ,  $M$  and  $N$  parameters and for methane and water are presented respectively in Figs. 7 and 8. The determination of possible singular points in the  $\alpha$ ,  $h_\alpha$  and  $C_\alpha$  functions was performed, for each component, according to (Eqs. (8)–(10)) and (Eqs. (A2)–(C2)); results are reported in Table 4.

According to the set of  $L$ ,  $M$  and  $N$  values considered [10,21], the alpha curves may or not present inflexion points, as it is shown in Table 4 and is illustrated in Figs. 7a and c for hexane; it can also be noticed that, since the alpha function parameters are tuned on saturation pressures, they provide quite similar attractive alpha curves for subcritical conditions, while they usually diverge in the supercritical temperature range (Fig. 7). For all components considered, Figs. 7b and 8b show that all the  $h_\alpha$  attractive functions involve inflexion points similar to those observed previously (Fig. 5) with the *subcritical* and *supercritical* Twu functions; hence, almost all the  $C_\alpha$  functions present abnormal extrema located in the temperature range commonly covered by industrial applications.

## 4. Conclusion

A theoretical analysis of the strengths and weaknesses of the Soave, Twu and Boston–Mathias alpha functions was performed using the Redlich–Kwong EoS in a wide range of reduced temperatures; a special attention was paid to the behavior of the first and second derivatives,  $h_\alpha$  and  $C_\alpha$ , appearing respectively in the enthalpy and the constant-pressure heat capacity. For the Soave function, it was shown that, not only the well known abnormal minimum of the alpha function  $\alpha(T_r)$  occurs at high temperatures, always beyond the current domain of industrial applications, but the  $h_\alpha$  and  $C_\alpha$  terms present consistent monotonous variations with increasing temperatures. Depending on the individual sets of  $L$ ,  $M$  and  $N$  parameters used, the Twu alpha function may provide an inflexion point leading to a zero value of the second derivative  $C_\alpha$ ; however, for all the investigated sets of parameters, the first derivative  $h_\alpha$  always presents inflexion points, leading to inconsistent extrema of the  $C_\alpha$  function for subcritical and supercritical conditions. Concerning the generalized Twu and Boston–Mathias models, the different sets of parameters used below and above the critical temperature always provide a continuous variation of the  $\alpha$  function and its first derivative at the critical point; regarding the second derivative, both models lead to abnormal extrema of the  $C_\alpha$  curves for supercritical conditions and inconsistent break points at the critical temperature. However, in the case of the Twu model, the  $C_\alpha$  function remains continuous at the critical point, whereas

the second derivative provided by the Boston model exhibits a real strong discontinuity.

The present study gave evidence that, for current industrial applications, there are no theoretical objective reasons to reject the Soave function, as well as for the modeling of vapor pressures or for the prediction of derived thermodynamic properties. The question of the accuracy of the experimental data modeling is discussed in the Part II of this work.

### List of symbols

$c, d$	parameters of the Boston–Mathias alpha function
$C_\alpha$	second derivative of the alpha term occurring in the heat capacity
$h_\alpha$	first derivative of the alpha term occurring in the enthalpy
$L, M, N$	parameters of the Twu alpha function
$m$	parameter of the Soave alpha function
$T$	absolute temperature

### Greek letters

$\alpha$	alpha function
$\omega$	acentric factor

### Subscript

$c$	critical property
extrem	extremum
inflex	inflexion point
$r$	reduced property
sub	subcritical property
sup	supercritical property

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