

# Analysis and prediction of the alpha-function parameters used in cubic equations of state



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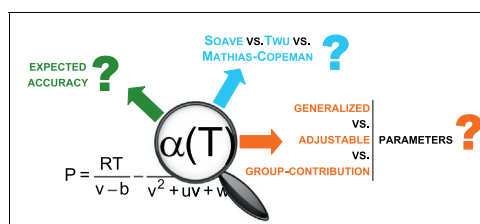
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## HIGHLIGHTS

- Various strategies to evaluate  $\alpha$  functions (cubic equations of state) are compared.
- Caloric and vapor–liquid equilibrium data were considered.
- New group-contribution methods are proposed to predict  $\alpha$ -function parameters.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The performance of two generalized alpha functions (Soave and generalized Twu functions requiring the acentric factor as input parameter) and two parameterizable alpha functions (Mathias–Copeman and Twu) incorporated in cubic equations of state (Redlich–Kwong and Peng–Robinson) is evaluated and compared regarding their ability to reproduce vapor pressure, heat of vaporization, liquid heat capacity, liquid density and second virial coefficient data. To reach this objective, extensive databanks of alpha function parameters were created. In particular, pitfalls of Twu-type alpha functions were evidenced and fixed. A new class of purely predictive alpha functions was derived by applying group-contribution (GC) methods to the prediction of alpha function parameters. The interest of such an approach is discussed and compared to another predictive approach (use of generalized alpha functions coupled with GC methods to predict the acentric factor).

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## 1. Introduction

Cubic equations of state (EoS) are commonly used to model and predict vapor–liquid equilibrium (VLE) and caloric data of pure components and mixtures flowing in chemical engineering processes. For pure species, most of these models can be written in

the general form:

$$P(T, v) = \underbrace{\frac{RT}{v-b}}_{\text{repulsive term}} + \underbrace{\frac{-a}{(v-r_1b)(v-r_2b)}}_{\text{attractive term}} \quad (1)$$

where

- $r_1$  and  $r_2$  are two universal constants of the EoS,
- $a$  is a temperature-dependent parameter reflecting the attractive intermolecular forces in the fluid,

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- $b$  is the so-called (molar) *covolume* of the considered molecule which depends on the critical properties of the fluid but is necessarily temperature-independent (Kalikhman et al., 2010).

For a given equation of state (i.e., for a given set of universal constants  $r_1$  and  $r_2$ ), the two pure-component cubic EoS parameters write

$$\begin{cases} a = \Omega_a R^2 T_c^2 \alpha(T) / P_c \\ b = \Omega_b R T_c / P_c \end{cases} \quad (2)$$

where  $T_c$  and  $P_c$  are the experimental values of the pure-fluid critical temperature and critical pressure, respectively. General expressions of the  $\Omega_a$  and  $\Omega_b$  universal coefficients can be derived by applying critical constraints to the cubic EoS (Privat et al., 2012):

$$\begin{cases} \eta_c = [\sqrt[3]{(1-r_1)(1-r_2)^2} + \sqrt[3]{(1-r_2)(1-r_1)^2} + 1]^{-1} \\ \Omega_a = (1-\eta_c \cdot r_1)(1-\eta_c \cdot r_2)(1-\eta_c)^{-1} [2-\eta_c(r_1+r_2)][3-\eta_c(1+r_1+r_2)]^{-2} \\ \Omega_b = \eta_c [3-\eta_c(1+r_1+r_2)]^{-1} \end{cases} \quad (3)$$

In Eq. (3),  $\eta_c$  is the critical packing fraction of the fluid. For illustration,  $\Omega_a$  and  $\Omega_b$  values associated with classical cubic EoS are reported in Table 1.

In Eq. (2),  $\alpha(T)$  is the so-called  $\alpha$  function which is temperature dependent (except for the Van der Waals EoS for which  $\alpha = 1$ ). Due to its definition, this function is equal to one at the critical temperature:  $\alpha(T_c) = 1$ . A wide number of models have been proposed to express this function (Valderrama, 2003), among those are

- The Soave (1972) function:

$$\alpha_{\text{Soave}}(T) = \left[ 1 + m \left( 1 - \sqrt{T_r} \right) \right]^2 \quad (4)$$

$T_r = T/T_c$  is the reduced temperature;  $m$  is a function of the experimental pure-component acentric factor the expression of which depends on the EoS choice<sup>1</sup>:

$$\begin{cases} m_{\text{RK}} = 0.480 + 1.574\omega - 0.176\omega^2 \\ m_{\text{PR}} = 0.37464 + 1.54226\omega - 0.26992\omega^2 \end{cases} \quad (5)$$

As an important feature of the Soave function, no adjustable parameter is needed. The mere knowledge of two experimental data ( $T_c$  and  $\omega$ ) allows estimating  $\alpha_{\text{Soave}}$  at a given temperature  $T$ . This function is used in particular in the PPR78 (Jaubert et al., 2010; Vitu et al., 2008), PR2SRK (Jaubert and Privat, 2010) and UMR-PR (Voutsas et al., 2004) predictive models (only for non-polar compounds in this last case).

- The generalized Twu  $\alpha$  function (gen. Twu) (Twu et al. 1995a,b):

$$\alpha_{\text{gen. Twu}}(T) = \alpha_0 + \omega(\alpha_1 - \alpha_0) \quad (6)$$

where

$$\begin{cases} \alpha_0 = T_r^{n_0(m_0-1)} \exp[l_0(1-T_r^{n_0 m_0})] \\ \alpha_1 = T_r^{n_1(m_1-1)} \exp[l_1(1-T_r^{n_1 m_1})] \end{cases} \quad (7)$$

This expression follows the formalism of the corresponding states as proposed by Lee and Kesler (1975). The parameters ( $l_0, l_1, m_0, m_1, n_0, n_1$ ) are universal constants (they are the same for all the compounds) and as a consequence, only depend on the considered EoS (see Table 2). Values of parameters in the subcritical region ( $T \leq T_c$ ) were determined by considering vapor pressures of argon, alkane compounds (from methane up to n-eicosane), cyclohexane and benzene (from triple points to critical points). For the supercritical region ( $T > T_c$ ), parameters were fitted to gas solubility data of methane and hydrogen in hydrocarbon liquids to reproduce Henry's constants.

Due to the use of different subcritical and supercritical parameter sets, the second derivatives of the generalized Twu  $\alpha$  function may exhibit inconsistent break points at the critical temperature (Neau et al., 2009a). Twu et al. however mentioned that "the continuity of the prediction of the properties at the critical point is maintained by making sure that the departure from the derived enthalpy and heat capacity properties (first and second derivatives with respect to temperature) are both smooth at the critical point" (Twu et al., 1995b).

As for the Soave function, there is no adjustable parameter in the  $\alpha_{\text{gen. Twu}}$  function. In addition to the temperature, the input parameters are as previous:  $T_c$  and  $\omega$ .

An adapted expression of the generalized Twu  $\alpha$  function is used in the VTPR predictive EoS developed by Ahlers and Gmehling (2002). In particular, the same set of parameters (fitted on vapor pressure, enthalpy of vaporization and liquid heat capacity data) is used in the sub- and supercritical regions (Diedrichs et al., 2006).

- The Mathias–Copeman (M–C) function (Mathias and Copeman, 1983):

$$\alpha_{\text{M-C}}(T) = \left[ 1 + c_1 \left( 1 - \sqrt{T_r} \right) + c_2 \left( 1 - \sqrt{T_r} \right)^2 + c_3 \left( 1 - \sqrt{T_r} \right)^3 \right]^2 \quad (8)$$

In this equation,  $c_1, c_2$  and  $c_3$  are adjustable parameters (they depend on the considered species) and are generally determined from VLE data. By setting  $c_2 = c_3 = 0$ , the original Soave function is obtained.

In their paper, Mathias and Copeman explained that the introduction of two new parameters (i.e.,  $c_2$  and  $c_3$ ) was "necessary to correlate the vapor pressure of highly polar substances like water and methanol".

This  $\alpha$  function is used in the well established PSRK (Holderbaum and Gmehling, 1991) and UMR-PR (Voutsas et al., 2004) predictive models (only for polar compounds in this last case).

- The Twu (1988) function (Twu, 1988):

$$\alpha_{\text{Twu(1988)}}(T) = T_r^{2(M-1)} \cdot \exp \left[ L \left( 1 - T_r^{2M} \right) \right] \quad (9)$$

where  $L$  and  $M$  are the two adjustable parameters.

- The Twu (1991) function (Twu et al., 1991):

$$\alpha_{\text{Twu(1991)}}(T) = T_r^{N(M-1)} \cdot \exp \left[ L \left( 1 - T_r^{N \cdot M} \right) \right] \quad (10)$$

To increase the flexibility of the Twu function there is one adjustable parameter more ( $N$ ) in the 1991 version than in the

**Table 1**

EoS parameters for three different cubic EoS (abbreviations are detailed in the section "notations").

EoS	$r_1$	$r_2$	$\Omega_a$	$\Omega_b$
VdW	0	0	27/64	1/8
Redlich–Kwong (RK) (Redlich and Kwong, 1949; Soave, 1972)	−1	0	0.42748	0.08664
Peng–Robinson (PR) (Peng and Robinson, 1976)	−1 − √2	−1 + √2	0.45724	0.07780

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