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The Soave, Twu and Boston–Mathias alpha functions in cubic equations of state. Part II. Modeling of thermodynamic properties of pure compounds

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ABSTRACT

Cubic equations of state (EoS) are commonly used for industrial applications, due to their simplicity in predicting pure compound and mixture thermodynamic properties in vapor and liquid phases. The accuracy of their predictions mainly depends on the choice of the attractive term $a(T)$ and numerous models were developed in literature for this purpose. Among them, the Soave and the Twu models have acquired a wide popularity, as well as the Boston–Mathias model commonly used for supercritical applications. However, most of the works concerned with the comparison of literature attractive terms only focuses on the representation of pure component saturation properties. In particular, the analysis of the respective influence of the EoS and the first and second derivatives of the alpha function on the modeling of enthalpies and heat capacities with respect to temperature and pressure, especially in the supercritical range, was never reported in literature. This is precisely the purpose of the present study.

1. Introduction

Cubic equations of state (EoS) are commonly used for industrial applications, due to their simplicity in predicting pure compound and mixture thermodynamic properties in vapor and liquid phases. The accuracy of their predictions mainly depends on the choice of the attractive term $a(T)$ and numerous models were developed in literature for this purpose. Among them, the Soave [1] and the Twu et al. [2] models have acquired a wide popularity, as well as the Boston–Mathias [3] model commonly used for supercritical applications. However, most of the works concerned with the comparison of literature attractive terms [4,5] only focuses on the representation of pure component saturation properties, mainly vapor pressures and liquid heat capacities [6]. In particular, the analysis of the respective influence of the EoS and the first and second derivatives of the alpha function on the modeling of enthalpies and heat capacities with respect to temperature and pressure, especially in the supercritical range, was never reported in literature.

In the part I of this study [7], a theoretical analysis of the Soave, Twu and Boston–Mathias alpha functions associated with the Redlich–Kwong equation [8] was performed in a wide range of reduced temperatures; special attention was paid to the behaviour of the first and second derivatives, h_α and C_α, appearing, respectively in the expressions of 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 occurs at high temperatures, always beyond the current domain of industrial applications, but also the h_α and C_α terms present consistent monotonous variations with increasing temperatures. Depending on the individual sets of L, M and N parameters, the Twu alpha function may or not present inflexion points leading to zero values of the second derivative C_α; but, for all the investigated sets of parameters, the first derivative h_α always presents inflexion points, providing inconsistent extrema of the C_α function for subcritical and supercritical conditions. Concerning the generalized Twu and Boston models, the different sets of parameters used below and above the critical temperature always allow continuous variations of the α function and its first derivative at the critical point; regarding the second derivative, both models lead to abnormal extrema of the C_α function for supercritical conditions and produce an inconsistent breakpoint at the critical temperature. However, in the case of the Twu model, the C_α function remains continuous at the critical point, whereas the Boston model exhibits a real strong discontinuity.

This second part deals with the modeling of saturation data and liquid enthalpies and heat capacities under pressure. An analysis of the influence of the various attractive terms with respect to

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temperature and pressure is performed for individual compounds, including hydrocarbons and polar substances.

2. Correlation of derived thermodynamic properties from the Redlich–Kwong equation

The calculation of thermodynamic properties of pure compounds is performed by using the Soave [1], Twu et al. [2] and Boston–Mathias [3] alpha functions associated with the Redlich–Kwong [8] EoS. In this framework, fugacity coefficients, required for the modeling of phase equilibria, and enthalpies and constant-pressure heat capacities are derived from the knowledge of the residual Helmholtz-free energy A^{res}:

$$\begin{aligned} A^{\text{res}} &= A(T,V,n) - A^{\text{ideal}}(T,V,n) \\ &= -nRT\int_{\infty}^{V}(z-1)\frac{dV}{V}, \quad z=\frac{PV}{nRT}=\frac{Pv}{RT} \end{aligned} \tag{1}$$

where A and A^{ideal} are respectively the Helmholtz-free energies of n moles of the real fluid and of the ideal gas at temperature T and for the total volume V; z is the compressibility factor of the real fluid, expressed for the Redlich–Kwong EoS as:

$$z=\frac{1}{1-\eta}-\frac{a(T)}{bRT}\frac{\eta}{(1+\eta)}, \quad \eta=\frac{b}{v} \tag{2}$$

$a(T)$ and b are respectively the attractive term and the covolume defined from the alpha function $\alpha(T)$ and the critical properties according to:

$$a(T)=a_c\alpha(T), \quad a_c=0.42748023\frac{R^2T_c^2}{P_c}, \quad b=0.08664035\frac{RT_c}{P_c} \tag{3}$$

From (Eqs. (1) and (2)), the expression of the residual Helmholtz-free energy A^{res} resulting from the use of the Redlich–Kwong equation is:

$$\frac{A^{\text{res}}}{nRT}=-Ln(1-\eta)-\frac{a(T)}{bRT}Ln(1+\eta) \tag{4}$$

The derivative of A^{res} with respect to the mole number n provides the logarithm of the fugacity coefficient φ:

$$\begin{aligned} \ln\varphi &= -\ln z+\left(\frac{\partial\left(A^{\text{res}}/RT\right)}{\partial n}\right)_{T,V} \\ &= z-1-Ln\,z-Ln(1-\eta)-\frac{a(T)}{bRT}Ln(1+\eta) \end{aligned} \tag{5}$$

while the derivatives with respect to temperature lead successively to the molar residual enthalpy h^{res}:

$$\begin{aligned} h^{\text{res}} &= h(T,V,n)-h^{\text{ideal}}(T)=RT(z-1)+\left(\frac{\partial\left(A^{\text{res}}/nT\right)}{\partial(1/T)}\right)_{V,n} \\ &= RT(z-1)-\frac{1}{b}\left(\frac{d(a/T)}{d(1/T)}\right)Ln(1+\eta) \end{aligned} \tag{6}$$

and to the molar residual constant-pressure heat capacity C_P^{res}:

$$\begin{aligned} C_P^{\text{res}} &= C_P(T,V,n)-C_P^{\text{ideal}}(T)=-\left[T\left(\frac{\partial P}{\partial V}\right)^{-1}\left(\frac{\partial P}{\partial T}\right)^{2}+R\right] \\ &\quad +\frac{\partial}{\partial T}\left(\frac{\partial\left(A^{\text{res}}/nT\right)}{\partial(1/T)}\right)_{V,n} \\ &= -\left[T\left(\frac{\partial P}{\partial V}\right)^{-1}\left(\frac{\partial P}{\partial T}\right)^{2}+R\right]-\frac{1}{b}\left[\frac{d}{dT}\left(\frac{d(a/T)}{d(1/T)}\right)\right]Ln(1+\eta) \end{aligned} \tag{7}$$

Hence, the modeling of thermodynamic properties, such as fugacity coefficients (Eq. (5)), enthalpies (Eq. (6)) or heat capacities (Eq. (7)), with respect to temperature and pressure, depends on the influence of the attractive functions weighted by $Ln(1+\eta)$, where η is the compacity (Eq. (2)) computed by means of the EoS.

The derivatives of the attractive term $a(T)$ occurring in the expressions of the residual enthalpy (Eq. (6)) and heat capacity (Eq. (7)) were defined as:

$$h_a=\frac{d(a/T)}{d(1/T)}, \quad C_a=\frac{d}{dT}\left(\frac{d(a/T)}{d(1/T)}\right)=\frac{dh_a}{dT} \tag{8}$$

They are correlated with the derivatives h_α and C_α of the alpha function $\alpha(T_r)$ analyzed in the first part of this study [7], as follows:

$$h_a=a_c h_\alpha, \quad h_\alpha=\frac{d(\alpha/T_r)}{d(1/T_r)} \tag{9}$$

$$C_a=\frac{a_c}{T_c}C_\alpha, \quad C_\alpha=\frac{dh_\alpha}{dT_r}=-T_r\frac{d^2\alpha}{dT_r^2} \tag{10}$$

The different literature alpha models considered in this work were divided into the following categories:

- The generalized versions, which only depend on the acentric factor ω; the corresponding expressions for the Soave (ω), Twu (ω) and Boston–Mathias (ω) functions are given in Table 1; for

Table 1
The Soave, Twu and Boston–Mathias alpha functions.

Soave	*Twu*	*Boston-Mathias*
$\alpha(T_r)=\left[1+m\left(1-T_r^{\gamma}\right)\right]^2$, $\gamma=0.5$	$\alpha(T_r)=T_r^{\delta}\exp\left[L\left(1-T_r^{\gamma}\right)\right]$ $\delta=N(M-1)$, $\gamma=NM$	*For* $T_r\le 1$: α from Soave *For* $T_r>1$: $\alpha(T_r)=\exp\left[c\left(1-T_r^{d}\right)\right]$
• *Soave(ω)* : $m=0.480+1.574\omega-0.176\omega^2$	• *Twu(ω)* : $\alpha=\alpha^{(0)}+\omega\left(\alpha^{(1)}-\alpha^{(0)}\right)$ *generalized L,M, N parameters (table 2)*	• *Boston-Mathias(ω)* : $d=1+m/2$, $c=m/d$ with: $m=0.480+1.574\omega-0.176\omega^2$
• *Soave(m)* : *Individual component parameters* (table 3)	• *Twu(LMN)* : *Individual component parameters* (table 3)	