DISCUSSION ON THE FUNCTIONAL FORM OF α-FUNCTIONS INVOLVED IN CUBIC EQUATIONS OF STATE.

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INTRODUCTION

Numerous modifications to the Van der Waals model have been presented over the years with the aim of representing with increasing accuracy the thermodynamics of complex systems. As a matter of facts, the most of those do not incorporate a substantial difference in the functional combination of attractive and repulsive forces, with respect to the original formulation introduced by Van der Waals. Although the analytical expressions of the repulsive and attractive terms proposed in literature do not correctly quantify the actual repulsive and attractive contribution to pressure, their sum results in a quantitative representation of fluid properties being sufficiently accurate to make their combination the "cornerstone of the generalized van der Waals theory". From the Van der Waals proposal, even the most successful two-parameter cubic equations of state (EoS) still express their attractive and repulsive term by introducing a parameter a, which is a measure of the attractive forces ("energy parameter") between molecules, and the parameter b, which is a measure of the size ("intrinsic volume" or "co-volume") of the molecules. The pure-component *a* energy parameter is directly proportional to the temperature-dependent alpha function $\alpha(T)$ which is a measure of how the a parameter deviates from its critical value. A wide variety of α-functions has been proposed over the past years. Those contain parameters which are adjusted according to different criteria: either over a whole set of components or for each specie ("generalized" versus "component-specific" α-function); either considering the whole temperature domain or specifically in the subcritical or supercritical regions ("overall" versus "domain-specific" α-function). Furthermore, among the mostly applied formulations, two different functional forms are identifiable: polynomial and exponential forms.

In this work, the popular component-specific Twu (1988) alpha function (denoted Twu88), which exhibits an exponential form has been selected to model Vapour-Liquid Equilibrium (VLE) behaviour of mixtures containing supercritical components. A key outcome of our work is that the use of the Twu88 α-function together with some sets of component-dependent parameters has resulted in the inaccurate VLE modelling of such mixtures, in spite of the use of advanced EoS/g^E mixing rules. A detailed examination of this issue has shown that the application of such sets of parameters entails the generation of abnormal deviations of the α-functions, when extrapolating at supercritical conditions. In parallel, the use of the simple generalized and polynomial Soave alpha function incorporated in the same advanced EoS/g^E mixing rules as previous, has led to very accurate results. In the basis of these counterintuitive results, it was attempted to understand how the use of an EoS coupled with a generalized alpha function (with no adjustable parameter) could induce better modelling results than an EoS coupled with a more flexible alpha function involving 2 adjustable parameters. It has been shown that the calibration of α-functions requires the imposition of constraints to the parameters under regression in order to guarantee consistent predictions of the derived thermodynamic properties (residual enthalpy, entropy, heat capacity …) at all temperatures (sub- or super-critical). On the basis of such conclusions, the Twu88 alpha-function has been re-parameterized for a large series of pure components (more than 900). In the light of the newly regressed parameters, a generalized Twu-type α function, performing better than Soave's α function, has been proposed. The use of this new generalized Twu alpha function has been used to model the VLE data of binary systems containing a supercritical component and has led to improved modelling results with respect to the use of the simple Soave alpha-function.

THE FUNCTIONAL FORM OF α-FUNCTIONS

One of the most influential contribution in the prediction of vapour pressures of non-polar and slightly polar pure compounds has been the introduction of the Soave *α-function* [1]. Over the years, further modifications have been introduced to this functional form, mainly aimed at improving the correlation of vapour pressures. However, most of the α-functions presented in literature have been developed without evaluating their predictive capability in the supercritical domain. It is nevertheless well acknowledged that one of the main targets, at the basis of the modifications to the Soave function, should consist in the improvement of the behaviour in the supercritical domain, in addition to that of increasing its accuracy in correlating vapour pressures of any fluid. The only attempt found in the literature, to improve the behaviour of α-functions in the supercritical region, consisted in optimizing the parameters of the function, separately, in the subcritical and supercritical domain. However, no modification has been found that introduces a novel functional form being able to improve the predictions in both the subcritical and supercritical regions, without distinguishing between parameters specifically applied in one of the two domains. To this modelling gap it should be associated the lack, in the literature, of specific theoretically based guidelines for defining an α-function that could guarantee consistent predictions of the derived thermodynamic properties, in the whole temperature range. With that respect, the purpose of this section is to present requirements that an α-function should fulfil.

As for the original Van der Waals equation of state, in contemporary cubic EoS the critical attractive parameter (a_c), the covolume b and the critical molar volume, v_c^{EoS}, can be determined by applying the so-called critical constraints recalled in Equ. (1).

$$\begin{cases} P_{c,exp} - P(T_{c,exp}, v_c^{EoS}) = 0 \\[2mm] \left(\dfrac{\partial P}{\partial v} \right)_T \bigg|_{\substack{T=T_{c,exp} \\ v=v_c^{EoS}}} = 0 \\[2mm] \left(\dfrac{\partial^2 P}{\partial v^2} \right)_T \bigg|_{\substack{T=T_{c,exp} \\ v=v_c^{EoS}}} = 0 \end{cases} \tag{1}$$

where $T_{c,exp}$ and $P_{c,exp}$ are the experimental critical temperature and pressure and where the critical molar volume is determined from the considered equation of state: $v_c^{EoS} = v(T_{c,exp}; P_{c,exp})$. The resulting critical energy parameter and covolume are usually expressed in terms of the EoS-dependent coefficients Ω_a and Ω_b:

$$\begin{cases} a_c = a(T_{c,exp}) = \Omega_a R^2 T_{c,exp}^2 / P_{c,exp} \\[2mm] b = \Omega_b R T_{c,exp} / P_{c,exp} \end{cases} \tag{2}$$

Differently from the covolume, necessarily temperature independent, at a temperature different from T_c the energy parameter, $a(T)$, is written in terms of its value at the critical point, a_c, and of the α-function:

$$a(T) = a_c \alpha(T) \tag{3}$$

It follows that $\alpha(T)$ is a non-dimensional factor which becomes unity at the critical temperature:

$$\alpha(T_c) = 1 \tag{4}$$

Moreover, to avoid non-physical negative values of the attractive term of cubic equations of state, an α-function should be a positive function at all temperatures:

$$\text{For all } T, \ \alpha(T) > 0 \tag{5}$$

At low temperatures, the average molecular kinetic energy is drastically reduced, resulting in a system where molecules are particularly prone to interact, upon collision. This explains the reason for which the EoS energy parameter should become increasingly important when temperature tends to zero. A decreasing, convex α-function, as the temperature approaches zero satisfies such requirements so that:

$$\begin{cases} \lim\limits_{T \to 0^+} \dfrac{d\alpha}{dT} < 0 \\[3mm] \lim\limits_{T \to 0^+} \dfrac{d^2\alpha}{dT^2} > 0 \end{cases} \tag{6}$$

The behaviour of the attractive parameter at infinite temperature is a question that remains open. For some authors the attractive term is zero at infinite temperature, for others, it takes a non-null finite value. If α-functions are obtained by forcing the EoS to reproduce properly selected experimental data, Colina et al. [2] clearly show that at the infinite temperature limit α-functions should exhibit negative values. As highlighted by themselves, finite negative values of the attractive term, at the infinite-temperature limit, would result from the necessity of counterbalancing the defects of the repulsive term, which at high temperature dominates over the negligible attractive one. Colina et al. also give proof that by assuming that: (i) at infinite temperature, the cubic EoS reduces to a hard-body equation of state and that (ii) the Van der Waals term RT/(v-b) correctly represents hard-body repulsions, the limiting value of α-function at infinite temperature should obviously be zero. As discussed by Abott and Prausnitz [3], there is however no theoretical evidence that the attractive part of cubic EoS cancels out at infinite temperature. Similarly, Sandler [4] merely alleges that at very high temperatures only the hard core part of the potential is important rather than the weaker (or *soft*) dispersive energies. Thus, both Abbott and Prausnitz [3] and Sandler [4] leave some uncertainty on whether the α-function at infinite temperature should assume a zero rather than finite value. Since no hard theoretical evidences have been found on this issue, we do not conclude about the theoretical limit of the α-function at infinite temperatures. In order to develop a new α-function we however practically need to quantify the limit of the function at infinite temperature. For such a practical reason, being aware of the irrelevance of the selected value attributed to this limit, we consider it equal to zero. We will also assume that the α-function is concave when T becomes infinite.

We can thus summarize our observations by:

$$\begin{cases} \alpha(T_c) = 1 \\[2mm] \forall\, T, \ \alpha(T) > 0 \\[2mm] \lim\limits_{T \to 0^+} \dfrac{d\alpha}{dT} < 0 \ \text{ and } \ \lim\limits_{T \to 0^+} \dfrac{d^2\alpha}{dT^2} > 0 \\[3mm] \lim\limits_{T \to +\infty} \dfrac{d\alpha}{dT} = 0 \ \text{ and } \ \lim\limits_{T \to +\infty} \dfrac{d^2\alpha}{dT^2} > 0 \end{cases} \tag{7}$$

In order to understand how do the derivatives of an α-function behave at intermediate temperatures, it is possible to consider the expression of the residual molar heat capacity at constant volume. Starting for the general form of a cubic EoS:

$$P = \frac{RT}{v-b} - \frac{a_c \cdot \alpha(T)}{(v - r_1 b)(v - r_2 b)} \tag{8}$$

One gets:

$$c_v^{res}(T, v) = -\frac{T a_c}{(r_1 - r_2) b} \ln\left(\frac{v - r_1 b}{v - r_2 b} \right) \left(\frac{d^2\alpha}{dT^2} \right) \tag{9}$$

From equation (9), it results that the presence of inflection points on an α-function at a specific temperature T* entails a zero $c_v^{res}(T^*)$:

$$\left(\frac{d^2\alpha}{dT^2}\right)\Bigg|_{T=T^*} = 0 \quad \Rightarrow \quad c_v^{res}(T^*,v) = 0 \quad \text{(for all v)} \tag{10}$$

As a result of the non-dependency from pressure of $d^2\alpha/dT^2$, at the temperature T* the fluid would be characterized by a unique heat capacity value (that of the corresponding perfect gas since $c_v^{res}(T^*)=0$) for any value of the molar volume, i.e. whatever the pressure would be [$c_v^{res}(T^*,v) = c_v^{perfect\ gas}(T^*)$]. In addition to this already unphysical condition, a further consequence has to be pointed out. Due to conditions in (7), we can state that the α-function is necessarily convex when T approaches zero or infinite. Consequently, the presence of one inflection point, on the curve representing the α-function, would involve the occurrence of, at least, a second inflection point at temperature T**. This would imply the existence of two temperatures, T* and T**, where the system would behave as a perfect gas, in terms of heat capacities ($c_v^{res}(T^*) = c_v^{res}(T^{**}) = 0$) and in correspondence of which all the isobars in a (c_v,T) plane would intersect. Such an absurd conclusion demonstrates that: (i) the α(T) must be a monotonically decreasing function of the temperature and (ii) $d^2\alpha/dT^2$ must be strictly positive at all temperatures.

To sum up, an α-function must verify:

$$\begin{cases} \alpha(T_c) = 1 \\ \alpha(T) > 0 \\ \dfrac{d\alpha}{dT} < 0 \\ \dfrac{d^2\alpha}{dT^2} > 0 \\ \lim\limits_{T\rightarrow+\infty} \alpha(T) = 0 \end{cases} \qquad \text{for all T} \tag{11}$$

In this work, the popular component-specific Twu alpha function (denoted Twu88) [5], which exhibits an exponential form has been selected to model VLE behaviour of mixtures containing supercritical components. Such an α-function, in which L and M are two adjustable parameters writes:

$$\alpha_{88} = T_r^{2(M-1)} \exp\left[L\left(1 - T_r^{2M}\right)\right] \tag{12}$$

L and M were fitted in order to check the constraints in Equ. (11). By doing so, inaccurate VLE modelling of such mixtures was obtained, in spite of the use of advanced EoS/g^E mixing rules. A detailed examination of this issue has shown that the application of the constraints described in Equ. (11) entails the generation of abnormal deviations of the α-function, when extrapolating at supercritical conditions.

It was however possible to fix this issue by imposing to the third derivative of α with respect to temperature to be negative. We can thus conclude that a necessary condition to get accurate results in the supercritical region with a cubic EoS is that:

$$\frac{d^3\alpha}{dT^3} < 0 \text{ for all T} \tag{13}$$

On the basis of such conclusion, the Twu88 alpha-function has been re-parameterized for a large series of pure components (more than 400). The parameters L and M were determined in order to check the mathematical constraints described in Equs. (11) and (13).

In the light of the newly regressed parameters, a generalized Twu-type α function, has been proposed.

RESULTS AND CONCLUSION

As stated in the previous section, parameters L and M could be correlated as a function of the acentric factor in order to propose a new generalized Twu-type α function. For the Peng-Robinson EoS [6-10], the following correlations were obtained:

$$\begin{cases} L_{PR} = 0.1208\omega^2 + 0.6066\omega + 0.0848 \\ M_{PR} = 0.1727\omega^2 - 0.2635\omega + 0.8873 \end{cases} \tag{14}$$

With such parameters, it was possible to predict with a very high accuracy the properties of many pure components. On a database of 400 pure components, the vapour pressures, the enthalpies of vaporization and the heat capacities were predicted with an accuracy of 1%, 2% and 4% respectively. Such deviations are much smaller than those observed with a Soave-type alpha-function, demonstrating the importance of respecting the constraints contained detailed in Equs. (11) and (13).

REFERENCES:

[1] Soave G., Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci.*, vol. 27, pp.1197–1203, 1972.
[2] Colina C., Santos J., Olivera-Fuentes C., High-temperature behaviour of the cohesion parameter of cubic equations of state. *High Temp.-High Press.*, vol. 29, pp. 525–532, 1977.
[3] Abbott M.M., Prausnitz J.M., Generalized van der waals theory: a classical perspective. *Fluid Phase Equilibria.*, vol. 37, pp. 29–62, 1987.
[4] Sandler S.I., The generalized van der Waals partition function as a basis for excess free energy models. *J. Supercrit. Fluids.*, vol. 55, pp. 496–502, 2010.
[5] Twu C.H., A Modified Redlich-Kwong Equation of State for Highly Polar, supercritical Systems. Proceedings of the International Symposium on Thermodynamics in Chemical Engineering and Industry, 1988, pp. 148.
[6] Peng D.Y., Robinson D.B., A new two-constant equation of state. *Ind. Eng. Chem. Fundam.*, vol. 15, pp. 59–64, 1976.
[7] Jaubert J.N., Mutelet F., VLE predictions with the Peng–Robinson equation of state and temperature–dependent k_{ij} calculated through a group contribution method. *Fluid Phase Equilib.*, vol. 224, pp. 285–304, 2004.

[8]   Vitu S., Privat R., Jaubert J.N., Mutelet F., Predicting the phase equilibria of CO_2 + hydrocarbon systems with the PPR78 model (PR EoS and kij calculated through a group contribution method). *J. Supercrit. Fluids.*, vol. 45, pp. 1–26, 2008.

[9]   Jaubert J.N., Privat R., Mutelet F., Predicting the phase equilibria of synthetic petroleum fluids with the PPR78 approach. *AIChE J.*, vol. 56, pp. 3225–3235, 2010.

[10] Jaubert J.N., Privat R, Relationship between the binary interaction parameters (k_{ij}) of the Peng–Robinson and those of the Soave–Redlich–Kwong equations of state. Application to the definition of the PR_2SRK model. *Fluid Phase Equilib.*, vol. 295, pp. 26–37, 2010.