

# An Improved Group Contribution Volume Translated Peng-Robinson Equation Of State

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## Abstract

The description of thermo-physical properties of pure components and mixtures, especially the equilibrium between two or more phases is of great importance for the design and simulation of chemical processes and many other applications.

The Volume Translated Peng-Robinson (VTPR) model provides an accurate means by which to calculate these properties for pure and mixed subcritical, as well as supercritical components, with reliable estimations for symmetric and asymmetric systems. However, VTPR requires group interaction parameters and currently the VTPR group interaction parameter matrix is small, as regression of these parameters using experimental data requires great care in order to obey all known boundary conditions. In contrast though, the modified UNIFAC group interaction parameter matrix, which has been continuously extended and improved since 1983 contains considerably more information and would be of great use in the VTPR method. The modified UNIFAC parameters however are unavailable for use in the VTPR method due to their temperature dependence, which leads to incorrect temperature extrapolations when used together with the VTPR mixing rule.

The new group contribution equation of state VGTPR introduces an excess Gibbs energy translation function into the mixing rule, which allows the combination of the volume translated Peng-Robinson EOS with the modified UNIFAC group contribution method, and allows the use of the large amount of information associated with modified UNIFAC. In the VGTPR method, the equality of  $g^E$  is obtained by iterative adjustment of the  $a$ -parameter of the EOS and is guaranteed at any temperature. A fixed reduced density of the pure components and the mixture is used for extension to supercritical conditions. The pressure difference between this state and the saturated state changes  $g^E$  only slightly due to the low pressure dependence of  $g^E$  in the liquid state. This model therefore allows the combination of the volume translated Peng-Robinson EOS with the modified UNIFAC method (with temperature dependent group interaction parameters).

The VGTPR method is fairly new and until now little has been done in terms of testing the method thoroughly. This work will present the re-derivation of the  $g^E$  translated mixing rule in an attempt to simplify the current algorithm and perform comprehensive tests on the VGTPR method, evaluating its performance utilizing the large amount of experimental data stored in the Dortmund Data Bank (DDB).

Keywords: Group-Contribution Equation of State (GCEOS), excess Gibbs energy ( $g^E$ ) mixing rule, VGTPR

## Literature Review

The main advantage of cubic equations of state is not so much in their ability to represent pure components but rather their applicability to fluid mixtures. Sengers *et al.* (2000) believe that representation of properties of fluid mixtures is the main, if not the only, purpose of cubic and generalized van der Waals equations of state and that when a pure fluid component is of interest, equations of this type are not the preferred method for representation. In any case, it is widely regarded that there is little room for improvement in the use of cubic equations of state for pure components as this field has had a vast amount of time and effort invested into it by past researchers. This has created an opinion that very little progress can be made with regard to pure component representation by equations of state; however, this is by no means the case when it comes to EOS use in multicomponent systems (mixtures).

In order to extend the pure component EOS models to mixtures, one can use the van der Waals one-fluid mixing rule. The one-fluid theory of mixtures is based on the assumption that the EOS for a mixture is the same as that for a hypothetical “pure” fluid that has EOS parameters which depend on the composition of the mixture. The relationship used to establish mixture parameters must describe the concentration dependence of these parameters and is commonly known as a mixing rule. Finding the correct cubic EOS mixture parameters ( $a_m$  and  $b_m$  in most cubic equations of state) is of utmost importance when representing a fluid mixture, in order to calculate accurate results. A number of different mixing rules have been developed, each one aiming at improving predictions of fluid mixtures using cubic equations of state. Generally, each new mixing rule improves on previous rules in certain areas, however, they fail in others. At present, one universal mixing rule is not available and research is continuing in order to establish a flexible and uncomplicated rule that could predict properties of most multicomponent systems with a reasonable level of accuracy.

The classical quadratic mixing rule is by far the most popular mixing rule mainly due to its simplicity and the relatively high level of accuracy achieved for mixtures containing non-polar or only slightly polar compounds. The origin of this mixing rule lies in basic statistical thermodynamics which is used to describe the composition dependence of the virial coefficients. The quadratic mixing rule suffers severe loss of accuracy in systems containing polar or associating compounds, and therefore has only a limited range of applicability. It also requires binary interaction parameters, which must be fitted to binary experimental data, in order to calculate the cross-term  $a_{ij}$ , and in fewer instances  $b_{ij}$ . Obviously, if these interaction parameters are not available, the use of this mixing rule is further limited.

In order to account for the shortcomings of the classical quadratic mixing rule, with respect to representing non-ideal systems, a number of advancements have been made. Many researchers developed composition-dependant combining rules which replaced the combining rules used to calculate the cross-terms in the original quadratic mixing rules. The mixing rule itself remains unchanged. Basically, all that was done here was the formulation of a composition dependant function to establish the cross terms and the introduction of more binary-interaction parameters. This obviously results in an increased level of complexity. While the composition-dependant combining rules do provide a simple method for extension of equations of state to mixtures containing non-polar or associating compounds, and do so with a satisfactory level of accuracy, they have been found to contain a serious defect which was discovered by Michelsen and Kistenmacher (1990) who investigated these composition-dependant combining rules. Sengers *et al.* (2000) explains the Michelsen-Kistenmacher problem as follows: *‘If a binary mixture with composition ( $x_1, x_2$ ) is treated as a ternary system with composition ( $x_1, x_2, x_3$ ), where the ternary mixture is formed by dividing component 2 into two pseudocomponents with identical properties, a different value for the parameter  $a$  will result. Therefore, the calculated properties will depend on the number of pseudocomponents, which is in contrast to experimental evidence’*. Many researchers attempted to overcome the Michelsen-Kistenmacher problem while maintaining the obvious

advantages of the composition-dependant combining rules. Mathias *et al.* (1991) and Twu *et al.* (1991) achieved this with some level of success by not only altering the combining rule but by also altering the form of the original quadratic mixing rule.

Highly non-ideal solutions (containing non-polar or associating compounds) have been described using excess Gibbs energy  $g^E$  (or activity coefficient) models with great success. Therefore, much effort has been dedicated to combining these models with equations of state in order to extend EOS applicability to non-ideal solutions, and consequently utilize the attractive features of both classes of models. The  $g^E$  of a solution can be calculated in two ways: with the use of an appropriate  $g^E$  model (most common) and with the use of an EOS via fundamental thermodynamic equations. Therefore, the EOS mixing rule composition-dependence for the liquid phase can be reflected by a desirable  $g^E$  model if the different expressions are matched as follows:

$$g_{\gamma}^E = g_{EOS}^E \quad (1)$$

The subscript  $\gamma$  indicates calculation by an activity coefficient model ( $g^E$  model) while the subscript *EOS* indicates calculation by means of an EOS. If one assumes a simple mixing rule for  $b_m$  applies (eg. linear mixing rule), the  $a_m$  parameter may be found by assuming that Equation (1) holds true.  $g_{\gamma}^E$  may be calculated by a number of different models (UNIQUAC, NRTL, UNIFAC, etc.) while  $g_{EOS}^E$  is calculated using a specific EOS and the following expression:

$$g_{EOS}^E = RT \left( \ln \varphi_m - \sum_{i=1}^{nc} z_i \ln \varphi_i \right) \quad (2)$$

Where  $nc$  is the number of components,  $z_i$  is the mole fraction of component  $i$  and  $\varphi_m$  and  $\varphi_i$  are the mixture and pure component fugacity coefficients respectively calculated (for pure components) by:

$$\ln \varphi = Z - 1 - \ln Z + \frac{1}{RT} \int_{\infty}^v \left( \frac{RT}{v} - P \right) dv. \quad (3)$$

where  $v$  is the molar volume,  $P$  is the system pressure (which is represented by an EOS as a function of  $v$ ),  $R$  is the universal gas constant and  $Z$  is the compressibility factor ( $= Pv/RT$ ). Equation (3) is also used to calculate  $\varphi_m$  as the mixture is assumed a pure fluid with pure component EOS parameters equal to  $a_m$  and  $b_m$ .

Vidal (1978) and Huron and Vidal (1979) were the first to use a  $g^E$  model to establish a mixing rule for an EOS in order to allow modeling of highly non-ideal systems. The Redlich-Kwong EOS was used by Vidal (1978), however the work of Huron and Vidal (1979) developed a generalized mixing rule for cubic equations of state. In order to successfully match  $g^E$ , an infinite pressure limit was imposed, which allowed the assumption that the molar volume of the fluid would be equal to the closest packing volume of the molecules due to the high level of compression. The  $b$  (co-volume) EOS parameter represents the closest packing volume of the molecules and therefore the following assumption could be made, which effectively removes the unknown fluid molar volume  $v$ :

$$\begin{aligned} v_i &= b_i \\ v_m &= b_m \end{aligned} \quad (4)$$

where  $v_i$  is the pure component molar volume of  $i$  and  $v_m$  is the molar volume of the mixture. In order to ensure that  $g^E$  is not infinite at infinite pressure the condition that the excess molar volume  $v^E$  is zero had to be imposed. This comes from investigating the following expression:

$$g^E = a^E + Pv^E \quad (5)$$

where  $a^E$  is the excess Helmholtz energy.

The general expression given by Huron and Vidal (1979) is:

$$a_m = b_m \left( \sum_{i=1}^{nc} \frac{a_{ii}}{b_i} z_i - \frac{g_\infty^E}{\Lambda} \right) \quad (6)$$

where  $\Lambda$  is a constant dependant on the EOS used and  $g_\infty^E$  is the excess Gibbs energy at infinite pressure. Equality (1) is assumed and the  $g_\infty^E$  term is calculated using a  $g^E$  model. The problem with this is that  $g^E$  is not independent of pressure, so calculations done on the same system at infinite and low pressure will produce different results.  $g^E$  calculated from the EOS is done at infinite pressure while  $g^E$  from a model is calculated using model parameters which are most commonly fitted using low pressure experimental data and is therefore effectively a low pressure calculation. In order to use equality (1) and use a  $g^E$  model to calculate  $g_\infty^E$  of Equation (6), the  $g^E$  model-parameters must be refitted using high pressure experimental data.

It soon became evident, following the work of Vidal and Huron and Vidal, that the  $g^E$  calculated from an EOS and from a  $g^E$  model needed to be linked at low pressure rather than at infinite pressure, so that the large amount of existing (low pressure) activity coefficient model-parameters could be utilized, therefore removing the need to measure data and refit model-parameters at elevated pressures. Mollerup (1986) was the first to move the field in this direction by matching the  $g^E$  from the EOS and an appropriate model at zero pressure. Michelson (1990) extended the idea proposed by Mollerup and matched the  $g^E$  at a reference pressure of zero using the SRK EOS. In doing so, the following expression was developed which in contrast to the Huron-Vidal mixing rule is not explicit:

$$\frac{g_0^E}{RT} + \sum_{i=1}^{nc} z_i \ln \left( \frac{b_m}{b_i} \right) = q(\alpha_m) - \sum_{i=1}^{nc} z_i q(\alpha_{ii}) \quad (7)$$

where  $g_0^E$  is the  $g^E$  at the zero reference pressure and can be calculated using an appropriate model.  $\alpha$  is a shortcut notation used to combine variables in the following way for pure component  $i$  and the mixture:

$$\alpha = \frac{a}{bRT} \quad (8)$$

$q$  is a function of  $\alpha$  and is given by:

$$q(\alpha) = -1 - \ln(u_0 - 1) - \alpha \ln \left( \frac{u_0 + 1}{u_0} \right) \quad (9)$$

$u_0$  is the reduced liquid phase volume at zero pressure:

$$u_0 = \left( \frac{v}{b} \right)_{P=0} \quad (10)$$

and may be expressed as a function of  $\alpha$  by solving the EOS at zero pressure for the smallest (liquid) root, which for the SRK EOS gives:

$$u_0 = \frac{1}{2} \left( \alpha - 1 - (\alpha^2 - 6\alpha + 1)^{1/2} \right) \quad (11)$$

valid for  $\alpha > 5.83$ .

Michelsen (1990) states that  $g^E$  model parameters are based mainly on binary mixtures at or near atmospheric pressure and under these conditions  $\alpha_i$  are far removed from the limiting value, with typical values (at the normal boiling point) ranging from 10 to 13. Michelsen (1990) investigated the behavior of the q-function within this range, and noticed that q varies almost linearly with respect to  $\alpha$ , therefore the q-function was approximated by the linear function:

$$q(\alpha) \approx q_0 + q_1\alpha \quad (12)$$

$q_0$  and  $q_1$  depend on the EOS used as the solution given by Equation (11) differs between equations of state. When substituted into Equation (7) the following mixing rule, commonly known as the Modified Huron-Vidal first-order mixing rule (MHV1) is obtained:

$$a_m = b_m \left( \sum_{i=1}^{nc} z_i \frac{a_i}{b_i} + \frac{1}{q_1} \left( g_\gamma^E + RT \sum_{i=1}^{nc} z_i \ln \left( \frac{b_m}{b_i} \right) \right) \right) \quad (13)$$

EOS dependant  $q_1$  is equal to -0.593, -0.53 and -0.85 for the SRK, PR and van der Waals EOS respectively.  $q_0$  cancels out on substitution and is therefore not important.

A Modified Huron-Vidal Second-Order mixing rule (MHV2) was later proposed by Dahl and Michelsen (1990) where a second order (quadratic) approximation is used to represent the q-function instead of the linear approximation (Equation (12)). This makes sense as the q-function is not perfectly linear and may be better approximated by a quadratic function, therefore producing better results. The quadratic approximation of q is:

$$q(\alpha) \approx q_0 + q_1\alpha + q_2\alpha^2 \quad (14)$$

Use of this approximation in Equation (7) does provide improved results over the MHV1 method, however there is added complexity as the resultant expression is not explicit and as stated by Michelsen (1990) *'the neatness associated with a simple explicit mixing rule is lost'*. The MHV2 equation is:

$$q_1 \left( \alpha_m - \sum_{i=1}^{nc} z_i \alpha_{ii} \right) + q_2 \left( \alpha_m^2 - \sum_{i=1}^{nc} z_i \alpha_{ii}^2 \right) = \frac{g_\gamma^E}{RT} + \sum_{i=1}^{nc} z_i \ln \left( \frac{b_m}{b_i} \right) \quad (15)$$

$q_1$  and  $q_2$  depend on the EOS used.  $q_1$  is equal to -0.478 and -0.4347 and  $q_2$  is equal to -0.0047 and -0.003654 for the SRK and PR EOS respectively.

Wong and Sandler (1992) proposed a new method to link the  $g^E$  model results with EOS computations in order to obtain a mixing rule for the EOS  $a$  and  $b$  parameters. Attempts to match the zero-pressure  $g^E$  were abandoned and the fact that excess Helmholtz energy ( $a^E$ ) is virtually independent of pressure was investigated, resulting in  $a^E$  calculated from an EOS being used to develop the mixing rule. There are two major advantages of using  $a^E$  instead of  $g^E$ . The first is that the assumption that  $v^E = 0$  is no longer required as when using  $g^E$  and the second, as stated already, is that  $a^E$  is not as strongly dependant on pressure as  $g^E$ . The basis of the work done by Wong and Sandler is summarized by the following expression:

$$a_{EOS}^E(T, P = \infty, z_i) = a^E(T, P = \infty, z_i) = a^E(T, P = low, z_i) = g^E(T, P = low, z_i) \quad (16)$$

The following argument is used in order to arrive at Equation (16): At sufficiently low pressures the  $Pv^E$  term of Equation (5) is very small. This implies that  $g^E$  is equivalent to  $a^E$  at low pressure.  $a^E$  is essentially independent of pressure (or density) and as a result  $a^E$  at low pressure is equivalent to  $a^E$  at infinite pressure. Therefore, the  $a^E$  of a system calculated at

infinite pressure using an EOS may be equated to the  $g^E$  of the system calculated using a  $g^E$  model, which is essentially a low pressure calculation (due to the original fitting of model parameters using low-pressure data). Calculation of  $a^E$  from a van der Waals type EOS at infinite pressure results in the following expression:

$$a_{\infty}^E = \Lambda \left( \frac{a_m}{b_m} - \sum_{i=1}^{nc} z_i \frac{a_i}{b_i} \right) \quad (17)$$

where  $\Lambda$  is a constant dependant on the EOS used. For the SRK and PR EOS  $\Lambda$  is equal to -0.693 and -0.623 respectively. Using Equation (16) Wong and Sandler were able to convert Equation (17) into the following form:

$$a_m = b_m \left( \sum_{i=1}^{nc} z_i \frac{a_i}{b_i} - \frac{g_{\gamma}^E(T, low P, z_i)}{\Lambda} \right) \quad (18)$$

The  $b_m$  parameter is not calculated by the simple linear mixing rule in the Wong-Sandler method, instead it was ensured that the second virial coefficient composition condition is satisfied. This resulted in the following expression for  $b_m$ :

$$b_m = \frac{\sum_{i=1}^{nc} \sum_{j=1}^{nc} x_i x_j B_{ij}}{1 + \frac{g_{\gamma}^E(T, low P, z_i)}{RT} - \sum_{i=1}^{nc} z_i \left( \frac{a_i}{b_i RT} \right)} \quad (19)$$

where  $B_{ij}$  is the second virial coefficient calculated as follows:

$$B_{ij} = b_{ij} - \frac{a_{ij}}{RT} = \frac{1}{2} \left[ \left( b_{ii} - \frac{a_{ii}}{RT} \right) + \left( b_{jj} - \frac{a_{jj}}{RT} \right) \right] (1 - k_{ij}) \quad (20)$$

$k_{ij}$  is a binary-interaction parameter that must be fitted to experimental data.

Holderbaum and Gmehling (1991) developed a group-contribution EOS that combined the SRK EOS and the UNIFAC method. The method is known as Predictive Soave-Redlich-Kwong (PSRK) due to its predictive abilities (as there was no introduction of new parameters which would require a fitting procedure, only existing UNIFAC group-interaction parameters are required). The PSRK equation can be used for predictions of VLE over a temperature and pressure range much wider than that possible with UNIFAC, and may also be easily extended for use in supercritical systems. The PSRK method makes use of the simple MHV1 mixing rule (Equation (13)), however the  $q_1$  value is changed to -0.64663 which produces more accurate results at elevated pressures and comes about due to the assumption of a constant packing fraction  $u$  ( $=v/b$ ) equal to 1.1 (based on low-pressure experimental data). Hence, Holderbaum and Gmehling (1991) states that PSRK is especially advantageous '*where use of a  $\gamma$ - $\phi$ -approach is difficult (i.e. when the real behavior of the vapour phase is unknown and not negligible) or inadequate (i.e. when supercritical components are present)*'.

Ahlers and Gmehling (2001) set out to improve on the work done by Holderbaum and Gmehling (1991), and develop an improved universal group contribution equation of state (GCEOS) which became known as the Volume Translated Peng-Robinson (VTPR) method. In order to eliminate the weaknesses of the PSRK method (poor results for saturated liquid densities and excess enthalpies), the method was derived from an improved CEOS by using the PR EOS with a volume translation instead of the SRK EOS and required group interaction

parameters were directly fitted to different thermodynamic properties. The volume translated PR EOS was linked to the UNIFAC group contribution method ( $g^E$  model) by means of the same mixing rule used for PSRK with slight modifications. The  $g^E$  calculated from a  $g^E$  model consists of a combinatorial part and a residual part as follows:

$$g_\gamma^E = g_{comb}^E + g_{res}^E \quad (21)$$

However, as described by Ahlers and Gmehling (2002), the combinatorial part may be neglected by altering the Flory-Huggins term  $\left( \sum_{i=1}^{nc} z_i \frac{b_m}{b_i} \right)$  of the PSRK equation and realizing that the PSRK method has two parameters of similar meaning, the co-volume  $b$  from the EOS and the relative van der Waals volume  $r$  from the UNIFAC method. The argument of Ahlers and Gmehling (2002) results in the following simplified mixing rule:

$$a_m = b_m \left( \sum_{i=1}^{nc} z_i \frac{a_i}{b_i} + \frac{g_{res}^E}{\Lambda} \right) \quad (22)$$

where  $\Lambda$  again is dependent on the EOS used and for the PR EOS is equivalent to -0.53087. The VTPR model can provide accurate predictions of pure component properties, phase equilibria and excess properties of subcritical, as well as supercritical systems which may be symmetric or asymmetric. It also has the advantage of improved density predictions due to the volume translation term; however, it does require the fitting of group interaction parameters to a large variety of experimental data which requires great care to obey the specific boundary conditions. This can be very tedious and time-consuming, which is why until now the parameter matrix of the VTPR method is still small and would require a great deal more effort to extend.

### VGTPR Model

Cubic equations of state contain their own temperature dependence and because of this, temperature dependent  $g^E$  model parameters (such as those of modified UNIFAC) cannot be used in the VTPR model. The combination of the temperature dependence in the EOS and the temperature dependence in a  $g^E$  model leads to erroneous results. In contrast to the VTPR method, the modified UNIFAC parameter matrix, which has been extended and improved since 1983 contains significantly more and very reliable group interaction parameters. It would therefore be a great benefit to incorporate the large amount of modified UNIFAC group-interaction parameters into the very successful VTPR model, hence removing the need to fit VTPR-specific parameters. This is what may be achieved by the new VGTPR method.

In the VGTPR method, a  $g^E$  translation function  $g_{trans}^E$  is introduced into the VTPR mixing rule (Equation(22)) as follows:

$$a_m = b_m \left( \sum_{i=1}^{nc} z_i \frac{a_i}{b_i} + \frac{g_{res}^E + g_{trans}^E}{\Lambda} \right) \quad (23)$$

The equality of  $g^E$  calculated from an EOS and the  $g^E$  model is obtained by iterative adjustment of the  $a_m$  parameter of the EOS and is guaranteed at any temperature. The translation function ensures  $g^E$  calculated by an EOS at the reference volumes is identical to the result of the  $g^E$  model, by effectively negating the double temperature dependency effect that produces incorrect results. The downside is that  $g^E$  in the EOS approach can only be calculated for subcritical components. It was therefore decided to calculate the equality not along the saturated vapour-pressure curve but at a certain fixed reduced density (reference density) of the pure components and the mixture. The pressure difference between this state and the saturated state changes  $g^E$  only slightly due to the low pressure dependence of  $g^E$  in the liquid state. The model is now applicable at sub- and supercritical conditions and

temperature dependent  $g^E$  model parameters regressed previously can be used in the EOS at any temperature. This model therefore allows combination of the volume-translated Peng-Robinson EOS with the modified UNIFAC method (with temperature dependent group interaction parameters).

This model was originally proposed and tested by Collinet *et al.* (2009) and was found to provide very accurate results. VGTPR was found to provide identical predictions to the modified UNIFAC model for vapour-liquid equilibria, excess enthalpies, activity coefficients at infinite dilution and solid-liquid equilibria. Using the reference volume, VGTPR was found to give very similar results to the PSRK model at subcritical conditions, however under supercritical conditions VGTPR was found to give markedly better results than PSRK.

The outlook of the VGTPR model is promising, however to date little research has been undertaken in the way of testing the model. Therefore, the purpose of this work is to extensively investigate the model using the large amount of experimental data already stored in the Dortmund Data Bank (DDB) with the idea of identifying any problems associated with the model and resolving these problems should they exist. Up until now, this work has not been initiated as a comprehensive review of the literature related to this topic has been undertaken.

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