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A Predictive Equation of State to Perform an Extending Screening of Working Fluids for Power and Refrigeration Cycles

Silvia Lasala, Andrés-Piña Martinez and Jean-Noël Jaubert

Abstract

This chapter presents the features of the *Enhanced-Predictive-PR78* equation of state (E-PPR78), a model highly suitable to perform “physical fluid screening” in power and refrigeration cycles. It enables, in fact, the accurate and predictive (i.e., without the need for its preliminary optimization by the user) determination of the thermodynamic properties of pure and multicomponent fluids usable in power and refrigeration cycles: hydrocarbons (alkanes, alkenes, alkynes, cycloalkane, naphthenic compounds, and so on), permanent gases (such as CO₂, N₂, H₂, He, Ar, O₂, NH₃, NO₂/N₂O₄, and so on), mercaptans, fluorocompounds, and water. The E-PPR78 equation of state is a developed form of the Peng-Robinson equation of state, which enables both the predictive determination of binary interaction parameters and the accurate calculation of pure fluid and mixture thermodynamic properties (saturation properties, enthalpies, heat capacities, volumes, and so on).

Keywords: thermodynamic cycle, pure working fluid, mixture, thermodynamic models, translated-E-PPR78

1. Introduction

Performance and design of closed power and refrigeration cycles are basically driven by the thermodynamic properties of their working fluids. This is the reason why, since the early 1900s, many researchers have been stressing over the importance of optimizing the working fluid of these cycles and of selecting a proper thermodynamic model to accurately calculate their properties.

Two approaches are currently applied to seek the optimal working fluid. The first strategy consists in considering a limited number of existing pure fluids, the “physical fluid screening.” Alternatively, authors apply a *product design* approach, consisting in considering the molecular parameters of the working fluid as optimization variables; the resulting optimal fluid is thus fictive and is named here “fictive fluid screening.”

The application of the “physical fluid screening” is preferably associated with the use of equations of state whose accuracy has been properly validated over experimental data of the considered set of existing fluids (see, e.g., [1–5]). The preferred modeling option lies in the use of multi-parameter equations of state such

as Helmholtz energy-based equations of state optimized by NIST (e.g., the GERG [6], the Span and Wagner [7], and so on), m-Benedict-Webb-Rubin (BWR) [8], Bender [9], and so on. Despite being highly accurate, these equations of state require the availability of a huge number of fluid-specific parameters, and their optimal values are thus provided by the model developer. An interesting chapter [10] has been recently published by Bell and Lemmon to spread the use of multi-parameter equations of state in the ORC community. However, at their current state of development, these models are thus not sufficiently flexible to be used in a screening approach extended to a population of hundreds of existing pure fluids and mixtures. For the same reason, the use of these multi-parameter models in a “fictive fluid screening” approach is inappropriate. To provide the reader with an order of magnitude, more than 1000 of fluids could be considered in this physical fluid screening procedure. The Design Institute for Physical Properties (DIPPR) currently provides accurate experimental data in a database (DIPPR 801) for 2330 pure fluids. Refprop 10.0 (NIST) [11] currently allows for the accurate representation of only 147 fluids.

To extend the range of considered fluids, studies present in the literature also consider the use of more flexible equations of state, that is, models characterized by a low number of parameters. If we focus on studies about closed power cycles, the equations of state, which have mainly been applied, are as follows: PC-SAFT-based model [12, 13] (which requires three molecule-specific parameters) in [14–16], BACKONE equation of state [17] (with four molecule-specific parameters) in [18], and the standard Peng-Robinson equations of state [19, 20] (with three parameters for each pure fluid) in [21–23]. These authors considered a different number of fluids. The one counting the highest considered number of fluids is the study by Drescher and Brüggemann [21], with 700 pure fluids. To our knowledge, all the other studies count less than 100 fluids (generally between 10 and 30). Peng-Robinson equation of state is currently the most flexible model to perform an extensive “physical fluid screening” of power and refrigeration working fluids. One of the main conclusions of authors who applied and compared different thermodynamic models (which is, unfortunately, rarely the case—we just found one study) is that the use of the Peng-Robinson equation of state is reliable in comparison with more accurate—but less flexible—multi-parameter equations of state [23].

Since 2004, Jaubert and co-workers have started publishing an improved version of the Peng-Robinson equation of state (version of the year 1978, PR78), the “Enhanced-Predictive-Peng-Robinson-78” (E-PPR78) [24–40]. Differently from PR78, this model is entirely able to **predict** the properties of mixtures *without the need for its preliminary calibration* over experimental data; moreover, the adjective *enhanced* has been juxtaposed to its previous name (PPR78) in 2011 [41] to highlight the **improved accuracy** in calculating **mixing enthalpies and heat capacities** (with respect to the original PPR78 model).

This model is widely used in the Chemical Engineering community but, inexplicably, remains unknown in the Energy Engineering one. The aims of this chapter are thus to present this model, to outline the proper way to apply it according to the latest advancements over pure fluid modeling [42–46], and to perform the screening of pure and/or multicomponent working fluids for power and refrigeration cycles.

2. From Peng-Robinson to E-PPR78 equation of state

The E-PPR78 model is an improved version of the equation of state published in 1978 by Peng and Robinson, the PR78 equation of state. This model has been

developed to allow for the accurate and predictive (i.e., without the need for its optimization over experimental data) application of the Peng-Robinson equation of state to multi-component mixtures. We thus start with introducing the forerunner PR78 equation of state:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)} \quad (1)$$

When applied to the i th pure component, a in Eq. (1) corresponds to the pure-component cohesive parameter, a_i , and b to its co-volume, b_i . We will refer to a and b to indicate the mixture cohesive and co-volume parameters. We will detail in the following section how to calculate pure fluid a_i and b_i (Section 2.1) and mixture a and b (Section 2.2). Before continuing, it is worth warning the reader of the fact that the original E -PPR78 model degenerates into the standard PR78 equation of state when considering pure fluids.

2.1 PR78: the application to pure fluids

When applied to pure fluids, the standard Peng-Robinson equation of state requires the definition of parameters a_i and b_i , calculated as reported in the following:

$$\left\{ \begin{array}{l} R = 8.314472 \text{ J mol}^{-1}\text{K}^{-1} \\ X = \left[1 + \sqrt[3]{4 - 2\sqrt{2}} + \sqrt[3]{4 + 2\sqrt{2}} \right]^{-1} \sim 0.253076587 \\ b_i = \Omega_b \frac{RT_{c,i}}{P_{c,i}} \text{ with: } \Omega_b = \frac{X}{X+3} \sim 0.07780 \\ a_i(T) = a_{c,i}\alpha_i(T) \text{ with } \left\{ \begin{array}{l} a_{c,i} = \Omega_a \frac{R^2 T_{c,i}^2}{P_{c,i}} \text{ and } \Omega_a = \frac{8(5X+1)}{49-37X} \sim 0.457235529 \\ \alpha_i(T) \text{ is the so-called } \alpha - \text{function} \end{array} \right. \end{array} \right. \quad (2)$$

The standard Peng-Robinson equation of state incorporates the Soave α -function [19, 47]:

$$\left\{ \begin{array}{l} \alpha_i(T) = \left[1 + m_i \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right]^2 \\ \text{if } \omega_i \leq 0.491 \text{ then } m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \\ \text{if } \omega_i > 0.491 \text{ then } m_i = 0.379642 + 1.48503\omega_i - 0.164423\omega_i^2 + 0.016666\omega_i^3 \end{array} \right. \quad (3)$$

However, in the last 4 years, two improved (i.e., thermodynamically consistent [42, 48] and very accurate) α -functions have been developed and published [44, 46]: a fluid-specific α -function and a generalized one, respectively, based on the model Twu91 [49] and Twu88 [50]. The application of the fluid-specific α -function Twu91 optimized in [46] guarantees the highest accuracy and requires three parameters (L , M , and N) for each pure fluid (reported by Pina-Martinez et al. [46] for 1721 molecules):

$$\alpha_i(T) = \left(\frac{T}{T_{c,i}} \right)^{N_i(M_i-1)} \cdot \exp \left[L_i \left(1 - \left(\frac{T}{T_{c,i}} \right)^{M_i N_i} \right) \right]^2 \quad (4)$$

The generalized version of Twu88 [46] requires, similar to the Soave α -function, the knowledge of the acentric factor of each pure fluid and takes the following form:

$$\begin{cases} \alpha_i(T) = \left(\frac{T}{T_{c,i}}\right)^{2(M_i-1)} \cdot \exp\left[L_i\left(1 - \left(\frac{T}{T_{c,i}}\right)^{2M_i}\right)\right]^2 \\ L_i(\omega_i) = 0.0925\omega_i^2 + 0.6693\omega_i + 0.0728 \\ M_i(\omega_i) = 0.1695\omega_i^2 - 0.2258\omega_i + 0.8788 \end{cases} \quad (5)$$

The alternative use of the three α -functions recalled above leads to different accuracies in the calculation of thermodynamic properties. A comparison is reported in **Table 1** between the PR equation of state incorporating the three different α -functions and pseudo-experimental data made available by DIPPR [51]. Piña-Martinez et al. also showed [46] that the modification of the α -function affects in a very negligible way the accuracy on volume calculations. To improve volumes, a further modification is required, as explained in Section 2.3.

2.2 From PR78 to E-PPR78: the application to mixtures

The application of the PR equation of state to a mixture requires the selection of mixing rules for calculating mixture cohesive and co-volume parameters, a and b . Classical Van der Waals one-fluid mixing rules are used in the original PR78 model:

$$\begin{cases} a(T, \mathbf{z}) = \sum_{i=1}^N \sum_{j=1}^N z_i z_j \sqrt{a_i(T) a_j(T)} (1 - k_{ij}) \\ b(\mathbf{z}) = \sum_{i=1}^N z_i b_i \end{cases} \quad (6)$$

The k_{ij} parameter is the so-called binary interaction parameter characterizing the molecular interactions between molecules i and j . The most accurate application of the original PR78 model requires the empirical optimization of the k_{ij} parameter over, at least, vapor-liquid equilibrium experimental data.

In 2004, Jaubert and Mutelet [24] proposed a model to *predictively* calculate the k_{ij} parameter by means of the application of a group contribution method. This method allows to estimate and predict the k_{ij} parameter by combining the molecular characteristics of elementary groups in which each molecule can be subdivided. This model is the most physically grounded model to determine the k_{ij} binary

α -Function	Soave, Eq. (3)	Generalized Twu88, Eq. (5)	Fluid-specific Twu91, Eq. (4)
MAPE on P^{sat} (1721 compounds)	2.8%	1.8%	1.0%
MAPE on $\Delta_{\text{vap}}H$ (1453 compounds)	3.1%	2.7%	2.9%
MAPE on $c_p^{\text{sat, liquid}}$ (829 compounds)	7.1%	4.1%	2.0%

Data have been collected from [46].

Table 1.

Comparison of the mean average percentage errors (MAPEs) calculated with PR incorporating either the Soave α -function or the generalized Twu88 α -function or fluid-specific Twu91 α -function.

interaction parameters of PR-78 equation of state, and its use is extremely recommended to predictively calculate thermodynamic properties of multi-component mixtures. The expression provided by this model to predictively calculate the binary interaction parameter is as follows:

$$k_{ij}(T) = \frac{-\frac{1}{2} \left[\sum_{k=1}^{N_g} \sum_{l=1}^{N_g} (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl} \left(\frac{298.15}{T/K} \right)^{\left(\frac{B_{kl}}{A_{kl}} - 1 \right)} \right] - \left(\frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j} \right)^2}{2 \frac{\sqrt{a_i(T)a_j(T)}}{b_i b_j}} \quad (7)$$

where a_i and b_i are the energy and co-volume parameters of the i th molecule, given in Eq. (2); N_g is the number of different groups defined by the method; and α_{ik} is the fraction of molecule i occupied by group k (occurrence of group k in molecule i divided by the total number of groups present in molecule i). A_{kl} and B_{kl} , the group-interaction parameters, are symmetric, $A_{kl} = A_{lk}$ and $B_{kl} = B_{lk}$ (where k and l are two different groups), and empirically determined by correlating experimental data. Also, $A_{kk} = B_{kk} = 0$. The inclusion of this predictive expression for k_{ij} in the PR78 equation of state results in the **Predictive-PR78 (PPR78)**.

It is worth recalling the historical development of the process of optimization of A_{kl} and B_{kl} provided by the model developers. These parameters have initially been optimized over only vapor-liquid equilibrium data of binary mixtures. The model resulting from the use of these so-optimized group contribution parameters is called PPR78 (Predictive-Peng-Robinson equation of state). Lately, authors recognized that the inclusion of enthalpy and heat capacity data in the optimization process does not affect the accuracy in modeling VLE properties but improves extraordinarily the accuracy in calculating enthalpies and heat capacities of mixtures. So, starting from the year 2011 [41], published A_{kl} and B_{kl} have been obtained by minimizing the errors between model calculations and experimental data relative to VLE, mixing enthalpy and heat capacity properties. The model resulting from the inclusion of these group contribution parameters is called **Enhanced-Predictive-PR78 equation of state (E-PPR78)**. The last optimized values of A_{kl} and of B_{kl} are reported in Table S1 of Supplementary Material of [39] for 40 molecular groups.

The optimization of these parameters has been performed over more than 150,000 experimental data and developed over more than 15 years. Even if preferable, that would be quite time-expensive if there was the need to re-optimize these group contribution parameters when changing any feature of the cubic equation of state (e.g., the α -function) or the cubic equation of state itself. Thankfully, it has been demonstrated [52] that it is possible to rigorously determine k_{ij} of any equation of state, knowing those of the original E-PPR78. In particular, it is possible to easily replace the Soave α -function, originally present in E-PPR78, with one of the improved functions presented in Section 2.1 (Eqs. (4) and (5)) and to use A_{kl} and B_{kl} parameters of the Soave-based E-PPR78 by applying, instead of Eq. (7):

$$k_{ij}(T) = \frac{-\frac{1}{2} \left[\sum_{k=1}^{N_g} \sum_{l=1}^{N_g} (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl} \left(\frac{298.15}{T/K} \right)^{\left(\frac{B_{kl}}{A_{kl}} - 1 \right)} \right] - \left(\frac{\sqrt{a_i^{\text{mod}}(T)}}{b_i} - \frac{\sqrt{a_j^{\text{mod}}(T)}}{b_j} \right)^2}{2 \frac{\sqrt{a_i^{\text{mod}}(T)a_j^{\text{mod}}(T)}}{b_i b_j}} \quad (8)$$

With respect to Eq. (7), this expression incorporates the pure component energy parameters calculated from the modified α -function. If we consider Twu α -function, we will thus use a_i^{mod} given by:

$$a_i^{\text{mod}}(T) = a_{c,i} \alpha_i^{\text{mod}}(T) \quad (9)$$

It is worth observing that for the systems for which the Soave α -function is already very accurate (i.e., *mean average percentage errors* of the order of 1% for saturation pressures and of 2% for vaporization enthalpies and liquid heat capacities), the k_{ij} in Eq. (7) (i.e., the standard E-PPR78 model, with the Soave function) is able to provide the best reproduction of mixture data. The alternative use of a more accurate α -function (which thus improves pure fluid calculations) and Eq. (8), to enable the use of original A_{kl} and B_{kl} group contribution parameters optimized with the original Soave-based E-PPR78, slightly deteriorates the results on mixtures (e.g., in the case of mixtures of alkanes). Clearly, the best would consist in re-optimizing all group contribution parameters using the best α -function directly in Eq. (7) instead of using the less-time-consuming Eq. (8) to derive the modified $k_{ij}(T)$ parameters. However, even adopting the simplified approach consisting in using Eq. (8), the predictive capability of this model remains very accurate for modeling

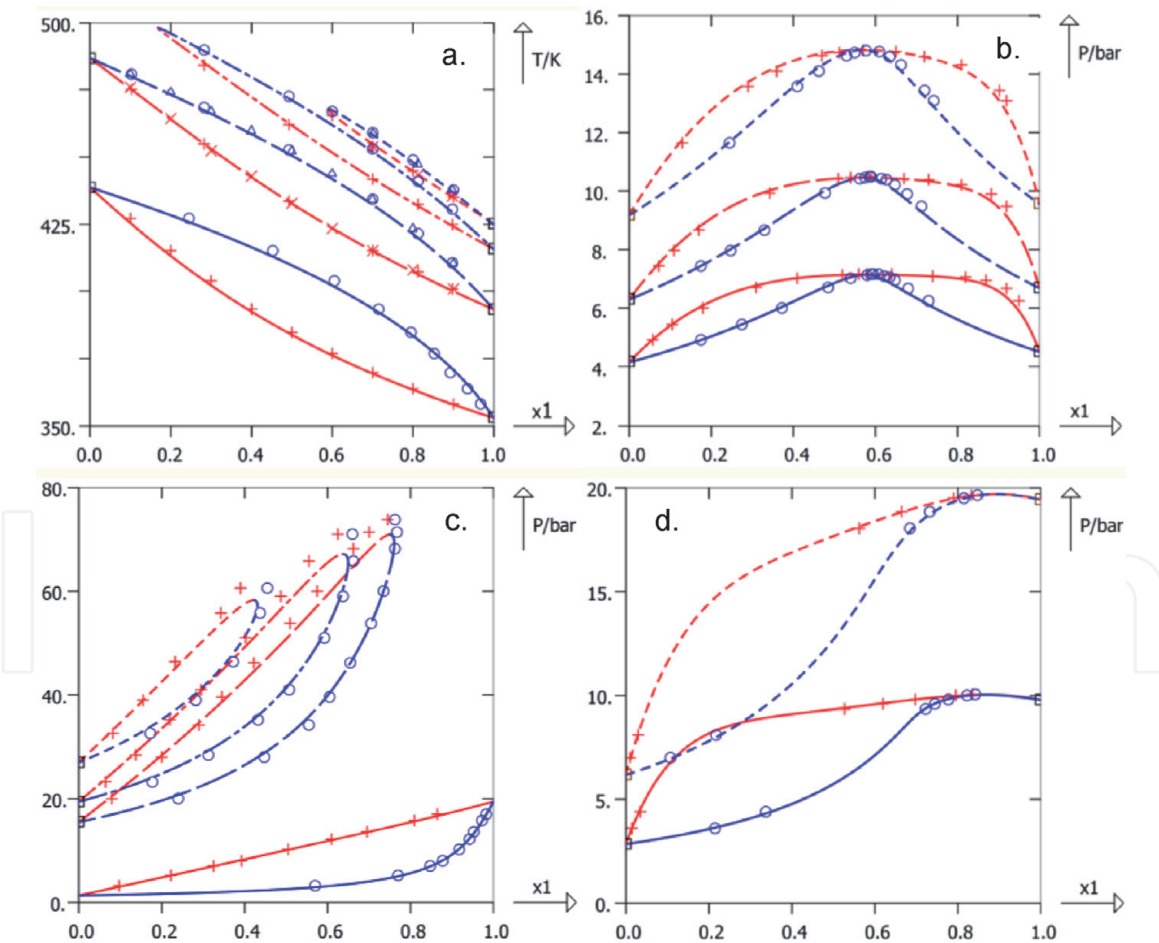


Figure 1.

Isobar vapor-liquid equilibrium phase diagrams for the system *n*-butane (1)–*n*-hexane (2) (a) and isothermal vapor-liquid equilibrium phase diagrams for the system 1-butene (1)–R610 (2) (b), CO₂ (1)–R134a (2) (c), R116 (1)–ethylene (2) (d). Lines represent calculations with E-PPR78 with Twu91 alpha-function, Eq. (4) (b). Bubble points are indicated in red, dew points in blue. Black points represent calculated pure component saturation pressures. (a) *P* (bar) = 10.132 (continuous line), 25.855 (long-dashed line), 32.75 (long- and short-dashed line), and 37.921 (short-dashed line); (b) *T* (K) = 312.92 (continuous line), 327.93 (long-dashed line), and 342.93 (short-dashed line); (c) *T* (K) = 252.95 (continuous line), 329.60 (long-dashed line), 339.10 (long- and short-dashed line), and 354.00 (short-dashed line); and (d) *T* (K) = 251.00 (continuous line) and 275.00 (short-dashed line).

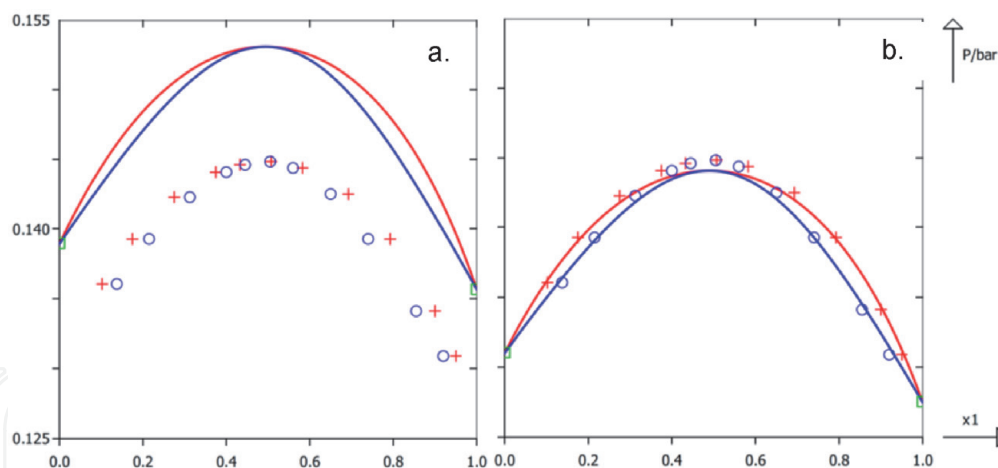


Figure 2. Isothermal VLE diagrams of the benzene (1)–cyclohexane (2) system, at 298.15 K. Lines represent calculations with standard E-PPR78 (a) and E-PPR78 with Twu91 alpha-function, Eq. (4) (b). Bubble points are indicated in red, dew points in blue. Green points represent calculated pure components saturation pressures.

closed power cycle working fluids and refrigerants (see the examples reported in **Figure 1**).

However, there are systems for which the Soave model is very inaccurate and the use of Twu α -function with Soave-based E-PPR78 A_{kl} and B_{kl} parameters highly improves results. By way of example, we present a pivotal binary mixture, benzene–cyclohexane, for which the standard PR equation of state (i.e., with the Soave α -function) does predict in a very inaccurate way of pure component saturation pressures. The original E-PPR78 equation of state, based on standard PR, is thus not very accurate in predictively modeling mixture saturation pressures because of the basic incapacity of the PR equation of state in modeling pure fluid properties (see in **Figure 2a**). However, if the Soave α -function is replaced with a more accurate α -function (given, e.g., by Eq. (4)) and if we then use Eq. (8) (with the Soave-based E-PPR78 A_{kl} and B_{kl} parameters reported in [39]) to represent benzene (formed by six groups CH_{aro}) and cyclohexane (formed by six groups $\text{CH}_{2,\text{cyclic}}$), we obtain the graph as shown in **Figure 2b**. The accuracy is thus strongly improved without the need of re-optimizing any parameter.

Considering the above remarks, we suggest the replacement of the Soave α -function with the Twu one, in E-PPR78, thus applying Eq. (8) and Soave-based E-PPR78 group contribution A_{kl} and B_{kl} parameters.

2.3 Volume correction

It is well known that one of the main limitations of cubic equations of state is their inaccuracy in high predicting liquid densities. P  neloux et al. [53] showed that it was possible to come up with this problem by adding a *translation term to the volume*. This translation consists in correcting the volume resulting from the resolution of the cubic equation of state (Eq. (1)) as follows:

- In case of pure fluids:

$$v_i^t(T, P) = v_i(T, P) - c_i \quad (10)$$

- In case of mixtures:

$$\begin{cases} v^t(T, P, z) = v(T, P, z) - c \\ c = \sum_i^{N_c} c_i \cdot z_i \quad (\text{linear mixing rule for } c) \end{cases} \quad (11)$$

In a recent publication, some accurate generalized (i.e., predictive) expressions for the translation term are optimized over 475 compounds, available in the DIPPR. For the Peng-Robinson equation of state, it is provided as follows:

$$c_i = \frac{RT_{c,i}}{P_{c,i}} (0.1975 - 0.7325 \cdot z_{RA,i}) \quad (12)$$

A databank of Rackett compressibility factors, z_{RA} , for 1489 components is available in Supplementary Material of [46]. The application of this translation has been observed to greatly improve the mean average percentage errors on calculated volumes. Considering the same 1489 pure fluids, the authors attested, in the same work, that the error in calculating the volume of the liquid phase at saturation condition is reduced from 8.7% (PR without translation) to 2.2% (PR with translation in Eq. (12)). If z_{RA} is not available, authors suggested the use of the following expression, where the translation term is only a function of the acentric factor.

$$c_i = \frac{RT_{c,i}}{P_{c,i}} (0.0096 + 0.0049 \cdot \omega_i) \quad (13)$$

Jaubert et al. [45] were able to demonstrate that entropy (s), internal energy (u), Helmholtz energy (a), constant pressure and constant volume heat capacity (c_p and c_v), vapor pressure (P^{sat}), and all properties change of vaporization ($\Delta_{vap}H$, $\Delta_{vap}S$, $\Delta_{vap}U$, $\Delta_{vap}A$, $\Delta_{vap}C_p$, and $\Delta_{vap}C_v$) of pure fluid properties are not influenced by a temperature-independent volume translation.

It can be thus deduced that the addition of a translation term and the modification of the α -function have unlinked effects: the utilization of a volume translation improves volume calculations without affecting the abovementioned thermodynamic properties, while the use of an improved α -function improves subcritical and supercritical properties without deteriorating density calculations (see Conclusion reported in Section 2.1).

The application of both the consistent-Two α -function (either Eq. (4) or Eq. (5)) and the volume translation in Eq. (12) results in the most accurate generalized cubic equation of state available in the literature.

For completeness, we would like to observe that, other than volume, also enthalpy and speed of sound are affected by the inclusion of a temperature-independent volume translation term (see [45]). However, the impact of such a translation on the calculation of enthalpy differences and of speed of sound is really negligible. In fact, it can be mathematically demonstrated from the use of relations presented in [45] that the enthalpy variation calculated with the translated cubic equation of state, Δh_t , and the one calculated with the nontranslated form, Δh_0 , are related by the following relation:

$$\frac{\overbrace{h_t(T_1, P_1) - h_t(T_2, P_2)}^{\Delta h_t}}{\underbrace{h_0(T_1, P_1) - h_0(T_2, P_2)}_{\Delta h_0}} = 1 - \frac{c_i \cdot (P_1 - P_2)}{\Delta h_0} \quad (14)$$

So, first, it can be observed that isobar enthalpy variations are not affected by the inclusion of a volume translation term. Moreover, it can be shown that, in general, for temperature and pressure conditions relevant for power and refrigeration cycle applications, the term $c_i \cdot (P_1 - P_2)/\Delta h_0$ is much lower than 0.001 for gaseous systems and lower than 0.005 for liquid systems. As regards the speed of sound, it can be mathematically derived that ratio between the speed of sound

determined with the translated cubic equation of state, w_t , and the one calculated with the nontranslated EoS, w_0 , is given by:

$$\frac{w_t(T, P)}{w_0(T, P)} = \sqrt{1 - \frac{c}{v(T, P)}} \quad (15)$$

which generally varies between 0.990 and 1.020 for liquid systems and is equal to 1.000 for vapor systems. These quantifications have been performed considering toluene, R134a, butane, propane, and ammonia.

3. Conclusion

Despite its simplicity and flexibility, E-PPR78 is a model that guarantees one of the most reliable predictive determinations of the thermodynamic properties of working fluids for power and refrigeration cycles. Being by definition a predictive model, its use is highly suggested to look for the best working fluid candidate over thousands of pure and multi-component fluids.

In this chapter, we presented the model and suggested to modify the Soave-based-original-E-PPR78 model by using the Twu α -function, to allow for the more precise representation of systems for which the Soave one is not sufficiently accurate. Finally, we recalled that the inclusion of a volume translation term in the E-PPR78 model highly improves the errors in the calculation of densities without affecting the rest of the, already accurate, properties.

Author details

Silvia Lasala*, Andrés-Piña Martinez and Jean-Noël Jaubert
 Université de Lorraine, CNRS, LRGP, Nancy, France

*Address all correspondence to: silvia.lasala@univ-lorraine.fr

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