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General correlation model for some physical properties of saturated pure fluids

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ABSTRACT

In this work, we use a general expression to accurately correlate the liquid density, the vaporization enthalpy, the surface tension, and the isobaric heat capacity of a saturated liquid *versus* temperature along the whole coexistence curve. The general expression used is the same for the four thermodynamic properties, and uses both critical and triple point values as reference. As representative examples of the use of the model, results are given for a set of 22 pure substances. We find that this general expression correlates the data with smaller or similar overall deviations when compared with other published models whose number of coefficients are the same or greater.

1. Introduction

There are several important practical applications that require an accurate knowledge of the behavior of thermodynamic properties *versus* temperature along the whole liquid–vapor coexistence curve, *i.e.*, along the saturation curve of fluids, from the triple point to the critical point. Different empirical correlations for every thermodynamic property have been proposed [1–3] so that it is very important to choose the appropriate model in order to properly correlate or predict the value of a given property for a given class of fluids or even for a particular fluid in a particular temperature range.

The most used correlations for thermodynamics properties along the saturation curve of fluids are based on the corresponding states principle [4], and they commonly use the critical point as a reference, and thus as an input property included in the design of the model. Despite the fact that these correlations give good results for a wide kind of fluids, they are not strictly applicable to complex substances as quantum and strongly associating fluids [3,4]. Moreover, they do not always give good results far from the critical point, *i.e.*, at low temperatures or near the triple point.

Following the idea of Torquato *et al.* [5,6] several authors have proposed using the triple point as an additional reference point [7–17], and this permits to have good accuracy in the whole temperature range at the (vapor + liquid) equilibrium. In particular, Román *et al.* [12] proposed the following reduced forms for a thermodynamic property and the temperature:

$$\psi^r \equiv \frac{\psi - \psi_c}{\psi_t - \psi_c} \quad \text{and} \quad t \equiv \frac{T - T_c}{T_t - T_c}, \tag{1}$$

where the superscript "*r*" means reduced value and the subscripts "*c*" and "*t*" mean critical and triple point values, respectively. Then they showed that, when this reduced form is applied to some properties such as the vaporization enthalpy, the difference between the coexistence saturation densities, and the surface tension, the corresponding data present an almost universal behavior. Moreover, they showed that those data can be correlated with a simple analytical expression that interpolates between the behaviors near the triple and the critical points [12].

The proposed expression takes into account that most properties have a singular behavior near the critical point, which can be described through a scaling law, predicted by renormalization-group (RG) theory [18] in the form [12]: $\psi^r \propto (1-t)^{\lambda}$, where λ is the critical exponent. According to RG theory, this critical exponent has a universal value for each property and a wide class of fluids.

In order to avoid the singular behavior near the critical point, Román *et al.* [12] showed that the term $\mathrm{Ln}[\psi^r(1-t)^{-\lambda}]$ behaves as a regular function which can be expanded in a Taylor series about $t = 0$. The expression finally proposed was [12]:

$$\psi^r = \exp\left[\sum_{n=1}^{\infty} a_n t^n\right](1-t)^{\lambda}, \tag{2}$$

where the a_n's are coefficients that must be determined [12].

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At a first step, equation (2) can be used by only considering the first term in the sum, when it has been shown [12] that the coefficient a_1 can be obtained from knowledge of the critical exponent λ and the slope of the property at the triple point. Therefore, the expression obtained has no adjustable parameters, but only includes parameters with physical meaning. Moreover, those parameters have practically the same value for certain properties, so that equation (2) permits the universal behavior of those properties to be reproduced.

The applicability and accuracy of this simple procedure was considered in Refs. [12,16]. Of course, when very accurate correlations are needed or when those two physical parameters are not known, the general expression must be used. For practical purposes, only a reduced number of terms, and hence a reduced number of adjustable coefficients, should be considered in equation (2). In this case an added advantage is that the same expression can be used for different properties, instead of the common procedure of using different expressions for each property.

In this work, we study the applicability and accuracy of equation (2) when it is used to correlate different properties for a set of fluids. In particular, we are interested in knowing whether equation (2) may be applicable to other properties not considered previously, and also in how this expression has to be used. We also compare the obtained results with those found when other well known correlation or predictive (*i.e.*, without using adjustable parameters) models are used, and then we determine how many coefficients are needed in order to obtain good accuracy for every property. It is not our aim to give the best coefficients for each property, model and fluid, but better to know if it is possible to have good accuracy by using a reduced number of coefficients.

In the use of equation (2), one also needs to know whether the critical exponent λ must be given a pre-fixed value or whether it is better to consider it as an adjustable coefficient. In the latter case, one needs to take into account that the scaling law is really the leading term of an extended scaling expression, so that when it is used to correlate experimental data the value obtained must be considered as an effective or apparent parameter [1,18].

We have selected four properties: the saturated liquid density, the vaporization enthalpy, the surface tension, and the inverse of the isobaric heat capacity of the saturated liquid, for which data along the whole coexistence curve for a set of 22 pure substances (mainly noble gases, alkanes, some refrigerants, and water) have been compiled from the NIST data bank [19].

The fluids and data used must be considered as representative examples of the performance of the model. In particular, the fluids were chosen as examples of well known fluids, for which data are available from different sources. The NIST data base was chosen because it permits to have the same number of data for each fluid and property, and because it can be used for everyone for free. Once the applicability and accuracy of the model would be shown, every research team could apply the model to their own data.

Figure 1 shows an illustrative example of the behavior of these four properties in reduced units. In particular, the vaporization enthalpy and the saturation liquid density behave similarly, the theoretical value of λ being around 0.38 and 0.35, respectively [1,2,12,16]. The surface tension has a clearly different behavior, the effective value of the critical exponent being around 1.23 [12,20]. Finally, we use the inverse of the heat capacity in order to avoid the divergence of the heat capacity of the saturated liquid at the critical point. Theoretically, this divergence presents a critical exponent which is the same as that of the isothermal compressibility [21,22]. The classical value of the critical exponent is 1, and in the 3D-Ising model is 5/4 [21,22]. From experiments the mean value is around 1.2 [21,22]. Nevertheless, as is shown below, we have found that this property has not the same behavior for different fluids, and the effective value of the λ parameter is different from the expected theoretical value.

2. Results

In all the cases we have considered the data given by the NIST data bank [19] for 22 common fluids (Ar, Kr, Xe, H_2, F_2, O_2, N_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16}, H_2O, NF_3, NH_3, and R123). We note that we have included two fluids, hydrogen and water, whose properties are generally difficult to fit or reproduce with commonly used models.

For each property we take a set of 100 data. The inputs needed for each model (critical and triple point data, and acentric factor) were also taken from NIST [19]. In each case we made a common fit procedure. To calculate the adjusted coefficients, we used the program *Mathematica* and the function NonlinearRegress [*data*, *expr*, *pars*,*vars*] in particular. It finds numerical values of the parameters *pars* that make the model *expr* give a best fit to data as a function of *vars* and provides diagnostics for the fitting.

Once all the fitting procedure is designed, we focus our attention on how many adjustable coefficients are needed for each mod-

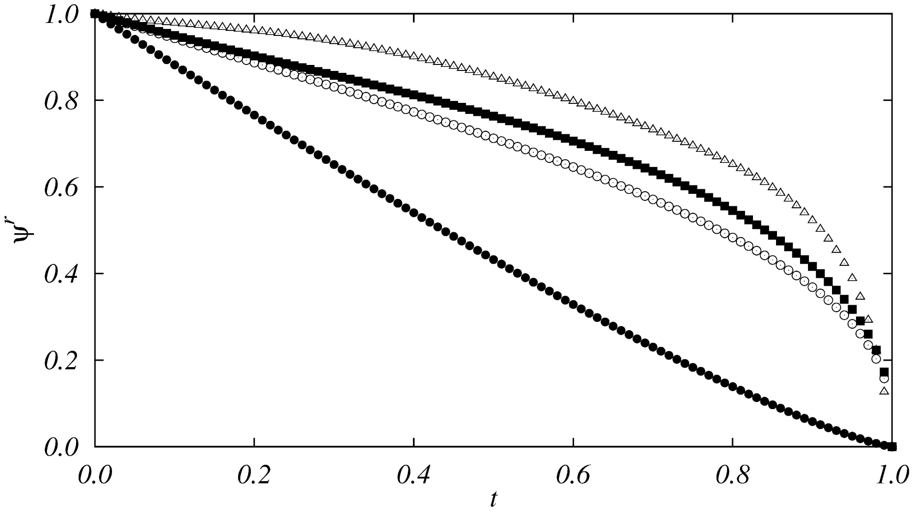

FIGURE 1. Reduced values *versus* the reduced temperature, equation (2), for: (○) the saturation density, ρ^r; (■) the vaporization enthalpy, H_v^r; (●) the surface tension, σ^r; and (△) the inverse of the isobaric heat capacity of propane.