

Development of an Extended Corresponding States Principle Method for Volumetric Property Predictions Based on a Lee–Kesler Reference Fluid

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The corresponding states principle (CSP) and the extended CSP have proven to be valuable tools in the prediction of properties of fluids and fluid mixtures. However, the accuracy of the application of these principles to property prediction is crucially dependent on the accuracy of the equation of state of the reference fluid or fluids involved. In this work, a new methodology of property prediction is developed and discussed. The revised extended corresponding states method, as developed by Marrucho and Ely, is combined with a reformulated (Teja-like) Lee–Kesler approach. The reformulated Lee–Kesler method is used to generate a pseudo-reference fluid, specific to each target fluid, which allows better mapping characteristics with any specified target fluid. This methodology is tested for the prediction of bulk volumetric properties of non-polar as well as polar fluids (specifically, alternative refrigerants). The results with different pseudo-reference fluids are compared with those of the original Lee–Kesler model and those obtained with *n*-propane as a single reference fluid. In the case of polar fluids, the prediction of properties is improved if the Taylor series expansion of the compressibility factor in the Lee–Kesler approach is affected in terms of the dipole moment rather than the acentric factor. The details of the combined “reformulated Lee–Kesler extended corresponding states” methodology are elucidated.

KEY WORDS: density; extended corresponding states; Lee–Kesler; alternative refrigerants.

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1. INTRODUCTION

Accurate methods for calculating thermodynamic and volumetric properties of pure substances and their mixtures are essential in engineering; efficient design, testing and suitability of equipment and processes need to be adequately ascertained, and the accurate knowledge of thermophysical properties becomes crucial. The scarcity of available experimental data, especially in regions “difficult” to measure, has mandated the development of theoretically based estimation tools.

The theoretically based estimation tools can broadly be categorized as: fluid specific correlation methods and generalized correlation methods. Highly accurate equations of state (EOS) developed from a wide range of experimental data fall under the first category of methods, where specific correlations (maybe of a generalized form) are formulated based on data for specific compounds. Many mathematical equations of state (EOS) formulations have been proposed with one of the more popular forms being the 32 term, modified Benedict–Webb–Rubin (MBWR-32) equation of state [1].

Of the many generalized correlation approaches that have been proposed, the three-parameter corresponding states principle (CSP) has proved to be the most powerful method for predicting properties of fluids and mixtures. Generally, this principle takes one of two forms: a one-fluid (single reference fluid) version that may incorporate extensions with shape factors or a multfluid (MFCSP) version that usually incorporates two reference fluids. The MFCSP was originally proposed by Pitzer et al. [2–4] and later modified by Lee and Kesler [5] to explicitly include a heavy reference fluid and more recently by Teja et al. [6, 7] to eliminate the need for a simple fluid as one of the references. Extensive reviews of the corresponding states principle as well as the Lee–Kesler model are found in the literature [8, 9].

It is noted, however, that irrespective of the sub-method in the CSP field, the reference fluid equations of state are crucial to the accurate prediction of the target fluid properties. In this work, we propose a combined reformulated Lee–Kesler extended corresponding states methodology for property prediction. The reformulated Lee–Kesler model is used to generate a pseudo-reference fluid with characteristics similar to the fluid of interest. This should enable a more efficient application of the extended corresponding states principle by providing a better mapping of the essential features between the fluid of interest and the newly generated pseudo-reference fluid.

It is also pointed out that in the majority of work in the literature, the Lee–Kesler or its reformulated version, reflects the first order Taylor series

expansion of the compressibility factor in terms of the acentric factor. In the case of alternative refrigerants, which are highly polar and with very similar acentricities, this leads to poor predictions. The perturbation of the compressibility and other thermodynamic properties in polar compounds may not be due to acentricity as much as to the difference in polarities or other factors. It is proposed in this work to perform the Taylor series expansion, in the case of polar fluids, in terms of the dipole moment. Both models are used to predict properties, and the results are compared with the original Lee–Kesler model, the reformulated Lee–Kesler model and the one-fluid extended corresponding states approach by using propane as the reference fluid. Similar methods, combining the size/shape and polarity effects were studied by Wu and Stiel [10] and Wilding et al. [11] as a combination of first and second order effects, which in our case do not lead to substantial improvements.

2. METHODOLOGY

In Teja's approach [6, 7], the compressibility factor of the target fluid is given by

$$Z(T^r, P^r) = Z^{(1)}(T^r, P^r) + \frac{\omega - \omega^{(1)}}{\omega^{(2)} - \omega^{(1)}} [Z^{(2)}(T^r, P^r) - Z^{(1)}(T^r, P^r)] \quad (1)$$

where ω is Pitzer's acentric factor and T^r and P^r are the reduced temperature and pressure of the target fluid. This equation may be considered to be a Taylor series expansion of the compressibility factor in terms of the acentric factor. In applying this model, the two reference fluids [denoted by superscripts (1) and (2)] are evaluated at different reduced volumes but the same reduced temperature as the target fluid. However, most of the high accuracy thermodynamic property models are expressed in a Helmholtz energy formulation and are as such explicit functions of temperature and molar density or molar volume as described in Eq. (2),

$$a_r = \frac{A - A^{\text{id}}}{RT} = f(T^r, V^r) \quad (2)$$

where a_r is the reduced dimensionless Helmholtz energy and A and A^{id} are the Helmholtz energies of the fluid at real and ideal conditions. Note, however, that the use of T^r and P^r as independent variables in Eq. (1) is not formally equivalent to the use of T^r and V^r , since the use of this last set of variables avoids the possibility of having the reference fluids in different states.

Pitzer-type correlations as expressed in Eq. (1) are based on empirical perturbation theory, and use the acentric factor to interpolate a given target fluid's properties between a spherical and a non-spherical reference. This can thus be extended to any general property, $\Psi(T^r, V^r)$, of the fluid [12],

$$\Psi(T^r, V^r) = \Psi^{(1)}(T^r, V^r) + \frac{\omega - \omega^{(1)}}{\omega^{(2)} - \omega^{(1)}} [\Psi^{(2)}(T^r, V^r) - \Psi^{(1)}(T^r, V^r)] \quad (3)$$

This formalism can then be applied to the Helmholtz energy, resulting in

$$a_r(T^r, V^r) = a_r^{(1)}(T^r, V^r) + \frac{\omega - \omega^{(1)}}{\omega^{(2)} - \omega^{(1)}} [a_r^{(2)}(T^r, V^r) - a_r^{(1)}(T^r, V^r)] \quad (4)$$

where a_r is defined in Eq. (2).

Equation (4) aides in the relatively simple application of the reformulated Lee–Kesler model to property models based on the Helmholtz energy formulation as well as to equations of state which are explicit in temperature and molar density. In particular, the application of this methodology to highly accurate equations of state, such as MBWR-32 or the Schmidt–Wagner type, may yield a pseudo-reference fluid with better matching characteristics. The functional form of the MBWR-32 equation is given as a polynomial,

$$P = \sum_{n=1}^9 C_n(T) \rho^n + \sum_{n=10}^{15} C_n(T) \rho^{2n-17} \quad (5)$$

and the temperature dependence of the $C_n(T)$ are summarized in Table I. The modalities of the construction of the pseudo-reference fluid involve the application of Eq. (3) to the coefficients, $C_n(T)$, in the reduced form given by

$$C_n(T^r) = C_n^{(1)}(T^r) + \frac{\omega - \omega^{(1)}}{\omega^{(2)} - \omega^{(1)}} [C_n^{(2)}(T^r) - C_n^{(1)}(T^r)] \quad (6)$$

The combination of the two reference fluids is effected through the combination of the coefficients of the equations of state that describe them. The coefficients now describe a new pseudo-reference fluid, which should have essential features more amenable for mapping with the target fluid. It is noted that the methodology described above for the combination of the two reference fluids imposes a constraint; it mandates that the equations of

Table I. Temperature Dependence of the MBWR-32 Coefficients

| | |
|---|---|
| $C_1 = RT$ | $C_9 = b_{19}/T^2$ |
| $C_2 = b_1T + b_2T^2 + b_3 + b_4/T + b_5/T^2$ | $C_{10} = b_{20}/T^2 + b_{21}/T^3$ |
| $C_3 = b_6T + b_7 + b_8/T + b_9/T^2$ | $C_{11} = b_{22}/T^2 + b_{23}/T^4$ |
| $C_4 = b_{10}T + b_{11} + b_{12}/T$ | $C_{12} = b_{24}/T^2 + b_{25}/T^3$ |
| $C_5 = b_{13}$ | $C_{13} = b_{26}/T^2 + b_{27}/T^4$ |
| $C_6 = b_{14}/T + b_{15}/T^2$ | $C_{14} = b_{28}/T^2 + b_{29}/T^3$ |
| $C_7 = b_{16}/T$ | $C_{15} = b_{30}/T^2 + b_{31}/T^3 + b_{32}/T^4$ |
| $C_8 = b_{17}/T + b_{18}/T^2$ | |

state used to describe the two reference fluids be of the same form (e.g., the MBWR-32 form). Moreover, in order to use Eq. (6), the two reference fluid equations of state have to be linear in the parameters. Note that Eq. (4) is valid for any kind of equation of state, but only in the case when the equation of state is linear in the parameters can Eq. (6) be derived.

Benedict, Webb, and Rubin [13] proposed similar internal mixing rules based on the van der Waals one-fluid idea that the mixture and the pure fluids should satisfy the same equation of state. These mixing rules, without adjustable parameters, were satisfactory for light hydrocarbon mixtures. One interaction parameter needed to be considered for asymmetric hydrocarbon mixtures, like methane and *n*-decane [14], hydrocarbon and carbon dioxide, and also for mixtures of polar and non-polar compounds, like nitrogen and chlorofluorocarbons or nitrogen and ammonia [15]. The behavior of this parameter depends strongly on the ideality of the system under study. A shortcoming of these mixing rules, as well as the methodology for the creation of the pseudo-reference fluid, arises from the fact that many pure component equations of state cannot be uniquely determined, and although these sets of constants are satisfactory for a pure fluid representation, they may lead to inconsistencies in the mixture calculation. This problem has been discussed by other authors [16], and it was found that it can be minimized if the generalised extended virial equations of state are written using parameters that are fluid characteristic, such as the acentric factor. Thus, the novelty in this work is to use the Lee–Kesler method as a mixing rule, instead of an empirical formulation of the acentric factor, to produce a reference fluid that is going to be used in the shape factor calculations.

In the case of alternative refrigerants, which are highly polar, the use of the acentric factor as the perturbation parameter may lead to poor predictions in properties, implying that the perturbation of the compressibility factor and other properties in polar compounds may not be due to acentricity as much as the difference in polarities or other factors. This can also

be inferred from studies of saturation pressures of alternative refrigerants of the same family [17]. It is observed that, within experimental error, these have very similar values, (within 10% of each other), implying that the acentric factors of these compounds do not vary much from each other, making it difficult to attribute the behavioral differences of these compounds to the acentric factor alone. It is thus proposed to effect the Taylor series expansion for any specific property, $\Psi(T^r, V^r)$, of polar compounds (e.g., alternative refrigerants) in terms of some polarity-dependent molecular property. The equation below elucidates the Taylor series expansion with the dipole moment of the compound as the perturbation parameter,

$$\Psi(T^r, V^r) = \Psi^{(1)}(T^r, V^r) + \frac{\mu - \mu^{(1)}}{\mu^{(2)} - \mu^{(1)}} [\Psi^{(2)}(T^r, V^r) - \Psi^{(1)}(T^r, V^r)] \quad (7)$$

where μ is the dipole moment.

This new pseudo-reference fluid is used to predict the density of selected fluids, using the shape factor approach [23]. This approach consists on calculating the properties of a fluid using a reference fluid. The mapping of the pVT surfaces of the two fluids is done using shape factors, which are weak functions of temperature and, in principal, density, that force the two fluids to conformality. In this work two paths are used to calculate the shape factors: the saturation boundary and critical isochore, and the Zeno line. The first method generates density-independent shape factors, which exhibit a good agreement with the exact shape factors in the subcritical region; in this region they are weakly density dependent. The shape factors are calculated along the saturation boundary, as proposed by Ely and Cullick [18]

$$\begin{aligned} P_j^{\text{sat}}(T_j) &= P_0^{\text{sat}}(T_j/f_j) h_j/f_j \\ \rho_j^{\text{sat},l}(T_j) &= \rho_0^{\text{sat},l}(T_j/f_j)/h_j \end{aligned} \quad (8)$$

where p_x^{sat} is the saturation pressure of the x fluid and $\rho_x^{\text{sat},l}$ is the saturated liquid density of the x fluid. The f_j and h_j are the scaling reducing ratios, and the subscripts j and 0 denote the working fluid and the reference fluid. Using the Frost-Kalkwarf-Thodos vapor-pressure equation [19],

$$\ln P^{r,\text{sat}} = B^* \left(\frac{1}{T^r} - 1 \right) + C^* \ln T^r + D^* \left(\frac{P^{r,\text{sat}}}{T^{r^2}} - 1 \right) \quad (9)$$

and the Rackett equation [20] for the saturation densities for both fluids, the following relationships are obtained for the shape factors, θ and ϕ [21],

$$\theta = \frac{1 - C_0^* + (1 - T_j^*)^{2/7} \ln(Z_j^c / Z_0^c) - \Delta B^* + \Delta C^* \ln T^* + B_j^* / T_j^*}{1 - C_0^* + B_0^* / T_j^*} \quad (10)$$

$$\phi = \frac{(Z_j^c)^{(1 - T_j^*)^{2/7}}}{(Z_0^c)^{(1 - T_j^* / \theta)^{2/7}}}$$

where X_i^* denotes the reduced parameter X of the Frost–Kalkwarf equation for the i fluid, $\Delta X = X_j^* - X_0^*$, and $X = C$ or B . In the supercritical region, ϕ is assumed to be constant and equal to the ratios of the critical compressibility factors of the reference, Z_0^c , and the target fluid, Z_j^c , and the critical isochores are assumed to be nearly linear, resulting in [22, 23]

$$\theta = \left(\frac{h_0(p_j^c - T_j^c \gamma_j^c) + (h_0 \gamma_j^c - \gamma_0^\sigma) T_j}{p_0^\sigma - \gamma_0^\sigma T_0^\sigma} \right) \frac{T_j^c}{T_0^c} \quad (11)$$

where the superscript σ indicates the isochore which intersects the reference fluid saturation boundary at $\rho_0^\sigma = \rho h_0$, $h_0 = Z_0^c \rho_0^c / Z_j^c \rho_j^c$ and $\gamma \equiv (\partial p / \partial T)_\rho \cdot \gamma^c$ for the target fluid j is calculated from the Frost–Kalkwarf equation.

The other method used to calculate shape factors is the Zeno line method which calculates the shape factors along the path $Z = 1$. The Zeno line has been thoroughly studied by several authors [24–26] and its corresponding states features are strikingly good, especially in the supercritical region. Usually the Zeno line is represented as [24]:

$$\frac{T}{T^z} + \frac{\rho}{\rho^z} = 1 \quad (12)$$

where the superscript z denotes the value of the property along the Zeno line. Several empirical correlations have been developed to calculate T^z and ρ^z based on different properties. In this work, the following correlations were used [24],

$$T^z = T^c(a + b\omega)$$

$$\rho^z = \rho^c(c + d\omega) \quad (13)$$

where a , b , c , and d are generalized constants equal to 3.499, 1.5345, 2.6961, and 1.6652, respectively. The calculation of the shape factors along this line is done in the usual form by equating the compressibility factor and the residual Helmholtz energy [21, 23].

Synoptically, the proposed methodology involves:

- (1) The construction of a pseudo-reference fluid using the reformulated Lee–Kesler model. The use of the perturbation parameter depends on the family of fluids being treated; i.e., acentric factor for non-polar compounds and dipole moment for polar compounds. The values for the dipole moment in the liquid phase are obtained from recent measurements by Mardolcar and Nieto de Castro [27].
- (2) Prediction of shape factors and volumetric properties of target fluids along two paths: saturation boundary and critical isochore, and the Zeno line.

3. RESULTS

The effectiveness of the new methodology is tested by comparing the densities of different hydrocarbons and alternative refrigerants. The densities used for the different fluids of interest for comparative studies are not experimental values, but are calculated using the MBWR-32 EOS within the temperature range of $0.3 \leq T^r \leq 1.8$ and pressure range of $0.1 \leq p^r \leq 30$. The equations of state yield density values that are within experimental error for most parts of the phase diagram under study. Tables II and III compare the density deviations using the standard ECST using *n*-propane as the reference fluid, the original Lee–Kesler method expressed by Eq. (1), and the proposed new methodology. In all tables AAD, BIAS and RMS are used and they are defined as

$$\begin{aligned}
 \text{AAD} &= \sum_i^{\text{NDP}} \text{ABS} \left(\frac{X_i^{\text{exp}} - X_i^{\text{calc}}}{X_i^{\text{exp}}} \right) \times \frac{100}{\text{NDP}} \\
 \text{BIAS} &= \sum_i^{\text{NDP}} \left(\frac{X_i^{\text{exp}} - X_i^{\text{calc}}}{X_i^{\text{exp}}} \right) \times \frac{100}{\text{NDP}} \\
 \text{RMS} &= \sqrt{\sum_i^{\text{NDP}} \left(\frac{X_i^{\text{exp}} - X_i^{\text{calc}}}{X_i^{\text{exp}}} \right)^2 \times \frac{100}{\text{NDP}} - \text{BIAS}^2}
 \end{aligned} \tag{14}$$

The choice of several combinations of reference fluids in the Lee–Kesler phase of the methodology is also investigated. In the case of hydrocarbons, two pseudo-reference fluids were constructed: one from methane and *n*-heptane, which could be used for the entire range of

Table IIIa. Summary of Density Deviations for Representative Hydrocarbons using the Saturation Boundary/Critical Isochore Method

| Reference Fluid | | ECST | | | Original LK | | | ECST+Lee-Kesler | | | | | | | | |
|-----------------|-----|-------|---------|------------------|-------------|------------------|---------|------------------|-------|--------|-------|-------|--------|-------|-------|--------|
| | | C3 | C1+n-C7 | Target-dependent | C1+n-C7 | Target-dependent | C1+n-C7 | Target-dependent | | | | | | | | |
| Target Fluid | NDP | AAD | RMS | BIAS | AAD | RMS | BIAS | AAD | RMS | BIAS | AAD | RMS | BIAS | | | |
| C2 | 616 | 1.363 | 0.765 | -1.363 | 0.926 | 5.727 | -0.08 | 0.866 | 7.211 | -0.139 | 1.440 | 1.014 | -1.440 | 0.991 | 0.949 | -0.983 |
| n-C4 | 616 | 1.059 | 1.121 | 0.116 | 0.435 | 0.351 | 0.421 | 0.356 | 0.448 | -0.014 | 1.100 | 1.017 | -1.099 | 0.817 | 1.005 | -0.271 |
| n-C5 | 616 | 1.879 | 2.439 | -0.523 | 0.611 | 0.857 | 0.342 | 1.308 | 1.768 | -0.403 | 2.308 | 1.747 | -2.307 | 2.130 | 2.525 | -2.119 |
| n-C6 | 614 | 2.212 | 2.583 | 0.662 | 1.869 | 3.01 | 0.994 | 1.972 | 3.139 | 0.821 | 2.206 | 2.806 | -1.665 | 2.189 | 2.968 | -1.134 |

Table IIIa. Summary of Density Deviations for Representative Hydrocarbons using the Zeno Line Method

| Reference Fluid | | ECST | | | Original LK | | | ECST+Lee-Kesler | | | | | | | | |
|-----------------|-----|-------|---------|------------------|-------------|------------------|---------|------------------|-------|--------|-------|-------|--------|-------|-------|--------|
| | | C3 | C1+n-C7 | Target-dependent | C1+n-C7 | Target-dependent | C1+n-C7 | Target-dependent | | | | | | | | |
| Target Fluid | NDP | AAD | RMS | BIAS | AAD | RMS | BIAS | AAD | RMS | BIAS | AAD | RMS | BIAS | | | |
| C2 | 616 | 0.297 | 0.612 | 0.234 | 0.926 | 5.727 | -0.08 | 0.866 | 7.211 | -0.139 | 0.245 | 0.398 | 0.189 | 0.118 | 0.171 | 0.057 |
| n-C4 | 616 | 0.251 | 0.462 | -0.015 | 0.435 | 0.351 | 0.421 | 0.356 | 0.448 | -0.014 | 0.411 | 0.377 | 0.398 | 0.244 | 0.329 | 0.107 |
| n-C5 | 616 | 0.412 | 1.105 | -0.357 | 0.611 | 0.857 | 0.342 | 1.308 | 1.768 | -0.403 | 0.547 | 0.798 | 0.401 | 0.872 | 1.316 | 0.306 |
| n-C6 | 614 | 1.759 | 2.807 | -1.173 | 1.869 | 3.01 | 0.994 | 1.972 | 3.139 | 0.821 | 0.963 | 1.436 | -0.256 | 1.198 | 1.737 | -0.467 |

Table IIIa. Summary of Density Deviations for Representative Refrigerants using the Saturation Boundary and Critical Isochore Method, with the Acentric Factor as the Perturbation Parameter

| Reference Fluid | ECST | | | Original LK | | | ECST + Lee-Kesler | | | | | | | | | |
|-----------------|------|-----------|--------------|-------------|--------------|-----------|-------------------|-----------|--------------|---------|--------|--------|--------|-------|--------|-------|
| | C3 | C2 + R125 | R125 + R152a | C2 + R125 | R125 + R152a | C2 + R125 | R125 + R152a | C2 + R125 | R125 + R152a | | | | | | | |
| Target Fluid | NDP | AAD | RMS | BIAS | AAD | RMS | BIAS | AAD | RMS | BIAS | AAD | RMS | BIAS | | | |
| R134a | 626 | 3.713 | 7.323 | 1.451 | 4.37 | 8.184 | -4.367 | 10.334 | 8.091 | -10.334 | 2.499 | 7.016 | -0.189 | 5.063 | 8.711 | 2.182 |
| R143a | 617 | 11.575 | 12.241 | 11.539 | 5.68 | 1.746 | -5.68 | 8.223 | 2.774 | 8.223 | 10.969 | 12.565 | 10.644 | 9.405 | 12.661 | 5.704 |

Table IIIb. Summary of Density Deviations for Representative Refrigerants using the Zeno Line Method, with the Acentric Factor as the Perturbation Parameter

| Reference Fluid | ECST | | | Original LK | | | ECST + Lee-Kesler | | | | | | | | | |
|-----------------|------|-----------|--------------|-------------|--------------|-----------|-------------------|-----------|--------------|---------|-------|--------|-------|--------|--------|-------|
| | C3 | C2 + R125 | R125 + R152a | C2 + R125 | R125 + R152a | C2 + R125 | R125 + R152a | C2 + R125 | R125 + R152a | | | | | | | |
| Target Fluid | NDP | AAD | RMS | BIAS | AAD | RMS | BIAS | AAD | RMS | BIAS | AAD | RMS | BIAS | | | |
| R134a | 626 | 1.900 | 8.774 | 0.081 | 4.37 | 8.184 | -4.367 | 10.334 | 8.091 | -10.334 | 1.809 | 8.487 | 1.222 | 3.144 | 9.475 | 0.269 |
| R143a | 617 | 9.188 | 11.973 | 9.159 | 5.68 | 1.746 | -5.68 | 8.223 | 2.774 | 8.223 | 9.707 | 12.252 | 9.687 | 11.872 | 20.345 | 9.335 |

hydrocarbons studied, and the other, a target-dependent reference fluid. This latter one is “created” by the combination of hydrocarbons that have one less and one more carbon atom than the specific target fluid. For example, in the case of ethane, the pseudo-reference fluid is constructed from methane and *n*-propane. In the case of refrigerants, the only two fluids that could be investigated were R134a and R143a due to non-availability of matching equations of state, which is a prerequisite for the construction of pseudo-reference fluids. Hence, two pseudo-reference fluids were analyzed: one from the combination of ethane and R125 (C2+R125); one fluid (C2) accounting for geometric effects and the other (R125) for polar effects, and the second from a combination of R125 and R152a, both polar fluids, but at the two extremes of the dipole moment spectrum for refrigerants in the liquid phase.

Table II (for hydrocarbons) and Table III (representative alternative refrigerants) show the comparative results of the present methodology. It is noticed that the deviations in densities obtained by using the new methodology with the Zeno line method and target-dependent reference fluids are considerably lower than the predictions of the standard ECST using *n*-propane as the reference fluid. This can be explained by the fact that shape factors calculated along the Zeno line are closer to the exact shape factors, especially above the critical point, than the ones calculated along the saturation boundary and critical isochore path.

The deviations in densities for the alternative refrigerants are seen to be high. Tables IV (a and b) show the deviations of the densities of alternative refrigerants when the Taylor series expansion of the compressibility factor in the Lee–Kesler approach is affected in terms of the dipole moment rather than the acentric factor. The perturbation of the properties of alternative refrigerants is better captured by the perturbation of the compressibility by the polarity (e.g., dipole moment) than the acentricity (e.g., acentric factor). In Figs. 1 and 2, the shape factors for R143a, using both extended corresponding states techniques and different pseudo-reference fluids, elucidate the major difference between these two methods above the critical temperature.

A side effect of this new methodology lies in the development of a method, which helps the study of the shape factor's behavior. Comparing Figs. 1 and 2, one can observe that the application of the ECST between the closer pseudo-reference fluid and the target fluid results in more regular shape factors, that is, a generally more ordered and conformal behavior of the shape factors. A comprehensive study of such regular shape factors could lead to simplified correlations for shape factor predictions encompassing large families of compounds, a facet which is under investigation.

Table IVa. Summary of Density Deviations for Representative Refrigerants using the Saturation Boundary and Critical Isochore Method, with the Dipole Moment as the Perturbation Parameter

| | | Original LK | | | | | | FKT | | | | | | | | |
|-----------------|-----|-------------|--------|---------|-------|------------|--------|---------|-------|------------|-------|--------|--------|-------|--------|-------|
| Reference Fluid | | C3 | | C2+R125 | | R125+R152a | | C2+R125 | | R125+R152a | | | | | | |
| Target Fluid | NDP | AAD | RMS | BIAS | AAD | RMS | BIAS | AAD | RMS | BIAS | AAD | RMS | BIAS | | | |
| R134a | 626 | 3.713 | 7.323 | 1.451 | 4.237 | 8.175 | -4.237 | 2.854 | 8.636 | 1.345 | 2.412 | 7.165 | -1.666 | 3.317 | 6.492 | -3.73 |
| R143a | 617 | 11.575 | 12.241 | 11.539 | 5.272 | 2.545 | -5.272 | 3.589 | 1.517 | 3.579 | 9.971 | 13.323 | 8.816 | 8.407 | 13.132 | 8.005 |

Table IVb. Summary of Density Deviations for Representative Refrigerants using the Zeno Line Method with the Dipole Moment as the Perturbation Parameter

| | | Original LK | | | | | | Zeno | | | | | | | | |
|-----------------|-----|-------------|--------|---------|-------|------------|--------|---------|-------|------------|--------|--------|-------|--------|--------|--------|
| Reference Fluid | | C3 | | C2+R125 | | R125+R152a | | C2+R125 | | R125+R152a | | | | | | |
| Target Fluid | NDP | AAD | RMS | BIAS | AAD | RMS | BIAS | AAD | RMS | BIAS | AAD | RMS | BIAS | | | |
| R134a | 626 | 1.900 | 8.774 | 0.081 | 4.237 | 8.175 | -4.237 | 2.854 | 8.636 | 1.345 | 2.056 | 7.11 | 0.473 | 1.418 | 6.6 | -0.071 |
| R143a | 617 | 9.188 | 11.973 | 9.159 | 5.272 | 2.545 | -5.272 | 3.589 | 1.517 | 3.579 | 10.348 | 13.392 | 9.687 | 10.252 | 13.076 | 9.999 |

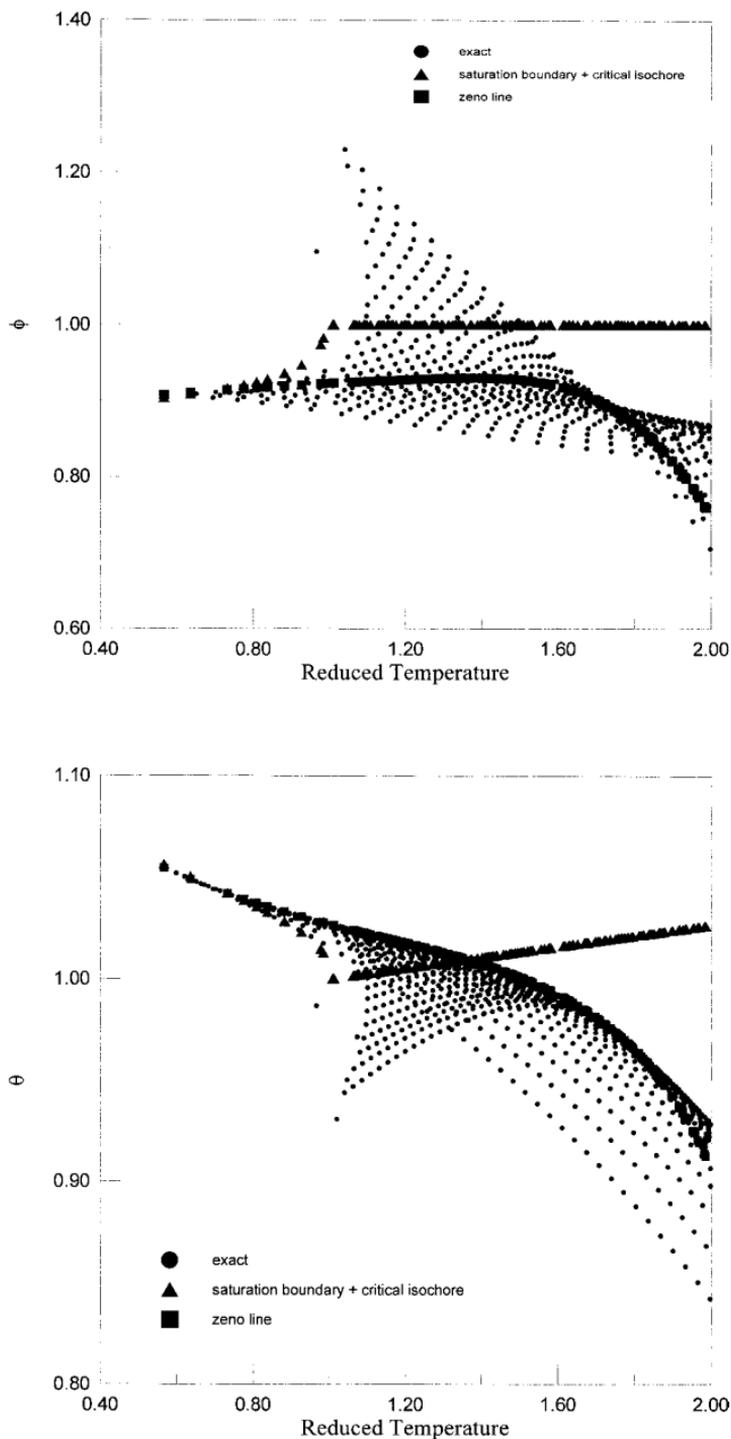


Fig. 1. Shape factors (a) ϕ and (b) θ for R134a using *n*-propane as reference fluid.

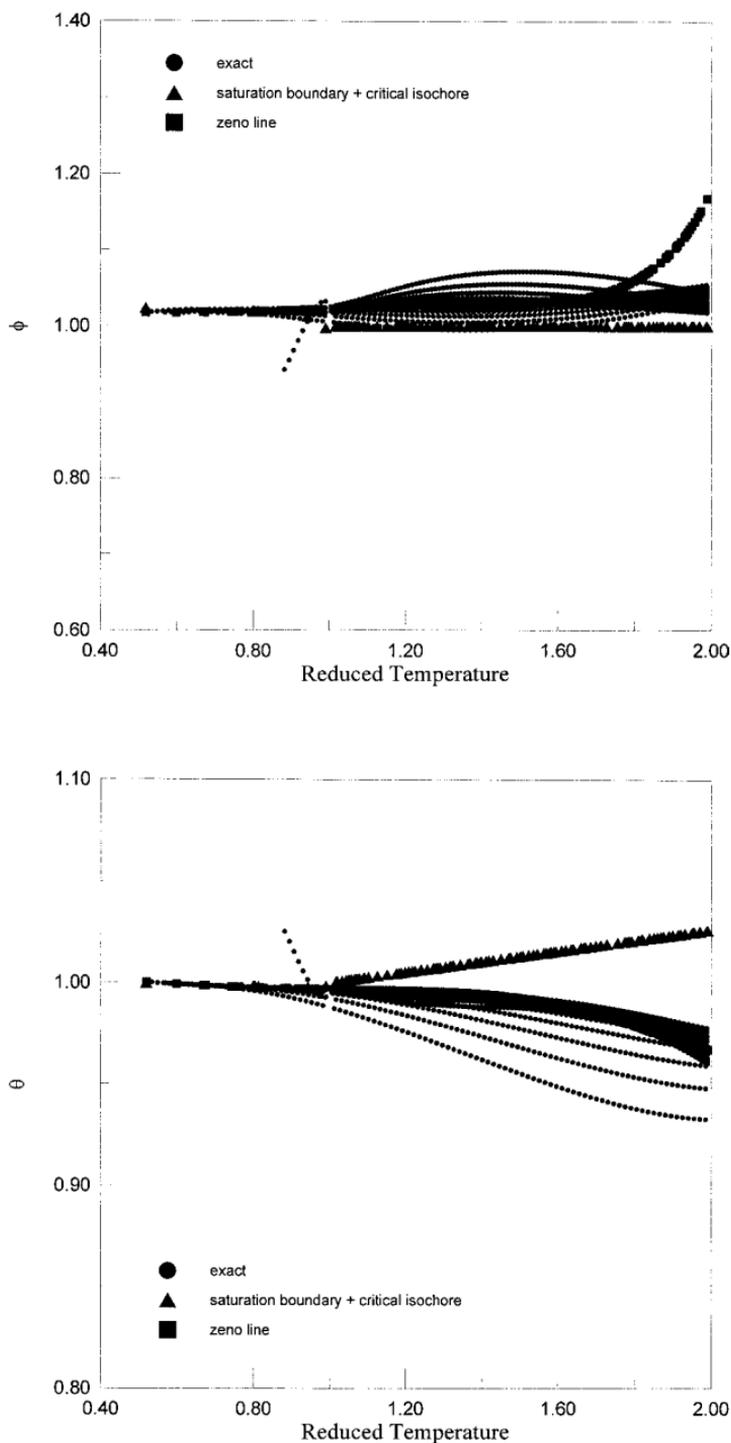


Fig. 2. Shape factors (a) ϕ and (b) θ for R134a using ethane and R152a as reference fluid.

4. SUMMARY AND CONCLUSIONS

In this work, a novel methodology is proposed that combines the reformulated Lee–Kesler method with the Extended Corresponding States theory. Preliminary studies of bulk volumetric properties with this technique exhibit generally better results than the existing one-fluid ECST using *n*-propane as the reference fluid or the Lee–Kesler approach in most cases. Future work will include the extension of the methodology to investigate its applicability to other fluid properties, e.g., heat capacity and enthalpy.

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