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The Prediction of High-Density Thermodynamic States Using Molecular Shape Factors[1]

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A new extended corresponding-states method for the prediction of high-density states for pure fluids is presented. The method incorporates the use of molecular shape factors. This approach requires accurate equations for the saturated-liquid density and the vapor pressure for the fluid in question. In addition, an equation of state for the vapor phase is also required. With this information, the molecular shape factors are calculated on the saturated-liquid line of the fluid being predicted, and they are assumed to be constant in the high-density, single-phase region along isotherms. This property prediction method is well suited for application to any fluid that has an equation of state valid in the vapor phase. Modern equations of state for nitrogen and oxygen were used to define properties of reference fluids in the development and testing of this new method. Experimental data for liquid ethylene were used to verify the accuracy of the new prediction method. Tests have shown that this approach predicts high-density data accurately to approximately six times the critical pressure and up to 85% of the critical temperature. The results of these tests are presented and discussed.

KEY WORDS: corresponding states; equation of state; molecular shape factor; vapor–liquid equilibrium.

1. INTRODUCTION

Numerous extensions of the corresponding-states principle for the prediction of thermodynamic states have been published in the literature. Among them is the work of Leach [1] incorporating the concept of molecular

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shape factors. The work reported here is an application of molecular shape factors to predict high-density thermodynamic states for pure fluids.

From statistical mechanics, it can be shown that two simple fluids will obey the same reduced equation of state when their intermolecular potentials have two adjustable parameters and a similar functional dependence on the molecular separation distance. For simple molecules, this is the case. For fluids which are complex and dissimilar, the above constraints cannot be met. Shape factors modify the critical parameters of dissimilar fluids to force exact correspondence on a reduced thermodynamic surface. These modified critical parameters, or pure-fluid pseudocritical parameters, allow the prediction of properties of a fluid using the equation of state of a selected reference fluid.

For a pure fluid i being predicted from the known properties of another pure fluid j, the shape factors (θ_{ij} and ϕ_{ij}) are defined to satisfy the following equations simultaneously:

$$Z_i(T_i, v_i) = Z_j(T_i/f, v_i/h) \tag{1}$$

$$\ln v_i(T_i, v_i) = \ln v_j(T_i/f, v_i/h) \tag{2}$$

where $f = (T_{ci}/T_{cj})\theta_{ij}$ and $h = (v_{ci}/v_{cj})\phi_{ij}$. The quantities f and h are referred to as the equivalent substance reducing ratios.

One common procedure for applying shape factors in the prediction of fluid states is to use a correlation for θ_{ij} and ϕ_{ij}. These correlations are usually of the form $\theta_{ij} = f_1(T_{ri}, v_{ri})$ and $\phi_{ij} = f_2(T_{ri}, v_{ri})$. Once the shape factors have been determined for a given T_{ri} and v_{ri}, Eq. (1) can be used to predict the pressure of fluid i. Generally the correlations for shape factors are developed for a group of fluids with similar molecular characteristics. Leach [1] used the normal hydrocarbon group, which is well defined by experiment. The development of correlations such as these requires substantial knowledge about several of the fluids in a fluid group. Such knowledge is not always available for fluids whose predicted properties are desired.

2. PREDICTION OF HIGH-DENSITY STATES

In the high-density liquid region of the thermodynamic surface, temperature and volume are not the natural variable pair to use in a corresponding-states calculation because of the steep slope $(\partial T/\partial v)_P$. Mathematical problems associated with this steep slope may often force the reference fluid (fluid j) point to be evaluated in the two-phase region where the equation of state is not valid. A more suitable variable pair to use in this region is temperature and pressure.

Equations (1) and (2) can be expressed in terms of temperature and pressure by defining a pressure shape factor, ψ_{ij}, as

$$\psi_{ij} = (P_{ri}/P_{rj}) = (Z_{cj}/Z_{ci})(\theta_{ij}/\phi_{ij}) \tag{3}$$

Using the pressure shape factor, Eqs. (1) and (2) can be rewritten as

$$Z_i(T_i, P_i) = Z_j(T_i/f, P_i/q) \tag{4}$$

$$\ln v_i(T_i, P_i) = \ln v_j(T_i/f, P_i/q) \tag{5}$$

where $q = (P_{ci}/P_{cj})\psi_{ij}$.

In general, shape factors are a function of temperature and volume. However, in Leach's [1] work with the normal hydrocarbons, it was found that for reduced volumes less than 0.5, the shape factors were independent of density. In this work, it was found that the shape factors for high-density liquid states where T_r is less than 0.85 and P_r is less than six are very weakly dependent on density. These limits vary somewhat, depending on the fluids involved in the prediction.

In this work, a method was developed to predict high-density thermodynamic states using shape factors calculated on the saturated-liquid curve of fluid *i*. This was done by modifying Eqs. (4) and (5) above as follows:

$$Z_i(T_i, P_{\sigma i}) = Z_j(T_i/f, P_{\sigma i}/q) \tag{6}$$

$$\ln v_i'(T_i, P_{\sigma i}) = \ln v_j(T_i/f, P_{\sigma i}/q) \tag{7}$$

where $P_{\sigma i}$ is the vapor pressure of fluid i at T_i and the prime denotes saturated liquid. The compressibiity factor Z_j and fugacity coefficient v_j were calculated using the reference-fluid equation of state. The compressibility factor Z_i was calculated on the saturated-liquid line at the given temperature T_i by

$$Z_i = P_{\sigma i}/(\rho_i' R T_i) \tag{8}$$

where ρ_i' is the saturated-liquid density of fluid *i*. The saturated-liquid fugacity coefficient for fluid i was determined by calculating the fugacity coefficient for the vapor state in equilibrium on the saturated-vapor curve. A vapor equation of state for fluid i was solved simultaneously with the vapor pressure equation at the temperature of the saturated-liquid state.

This procedure requires a vapor pressure equation, a saturated-liquid density equation, and an equation of state valid for vapor states near saturation for the fluid being predicted (fluid i). These equations are typical for pure fluids whose thermodynamic property formulations are built around a Martin–Hou equation of state. The accuracy of available information depends upon the source, but for the fluids used in this work, reliable equations and data were available.

3. TESTING THE METHOD

The above method of predicting high-density states was applied to ethylene, and the results were compared to the experimental data for ethylene of Calado et al. [2] and Straty [3]. The shape factors θ_{ij} and ψ_{ij} were determined by simultaneous solution of Eqs. (6) and (7). The prediction method was tested using two different reference fluids, nitrogen and

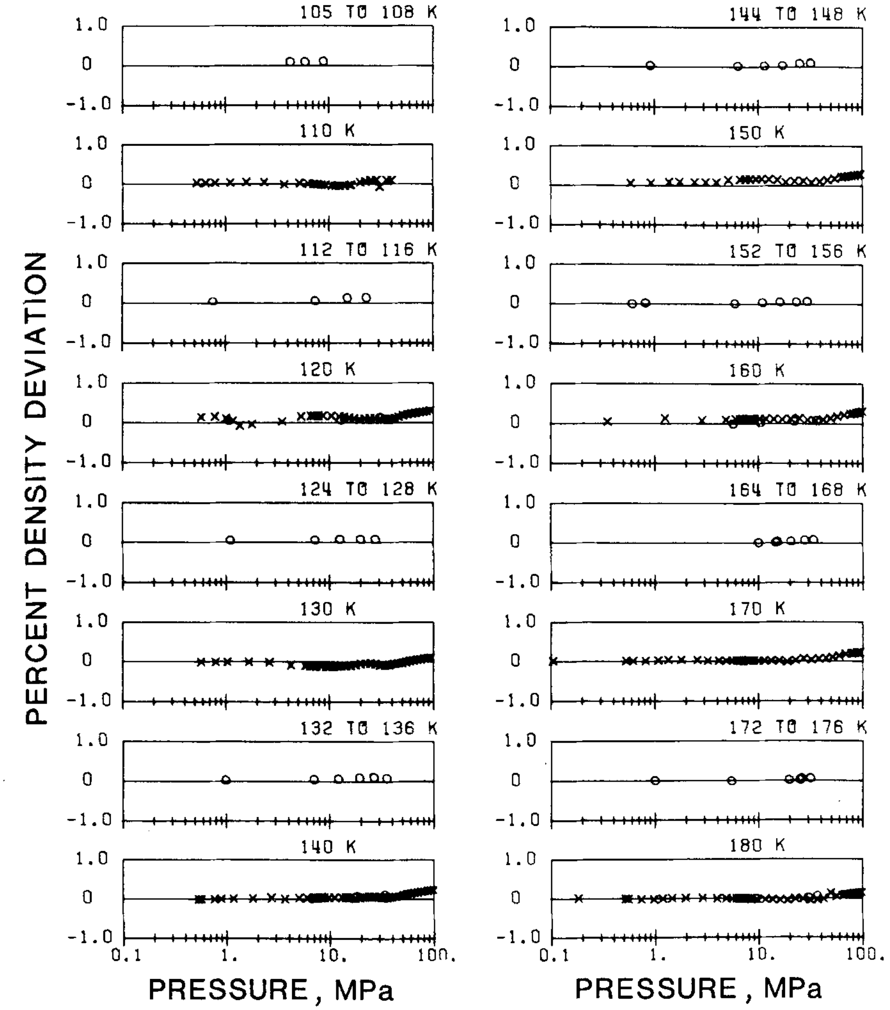

Fig. 1. Comparison of predicted ethylene liquid density using high-density shape factors to experimental data. The reference fluid is oxygen. The data are from (X) Calado et al. [2] and (O) Straty [3].

oxygen. The equation of state for nitrogen was published by Jacobsen et al. [4]. The oxygen equation of state was done by Stewart et al. [5] and agrees closely with the equation of Schmidt and Wagner [6] for the fluid states used in this study. The vapor pressure and saturated-liquid density equations used for ethylene were those of Jahangiri et al. [7]. The equation of state for ethylene of Jahangiri et al. [7] was used for the calculation of the saturated-vapor fugacity coefficient as described above.

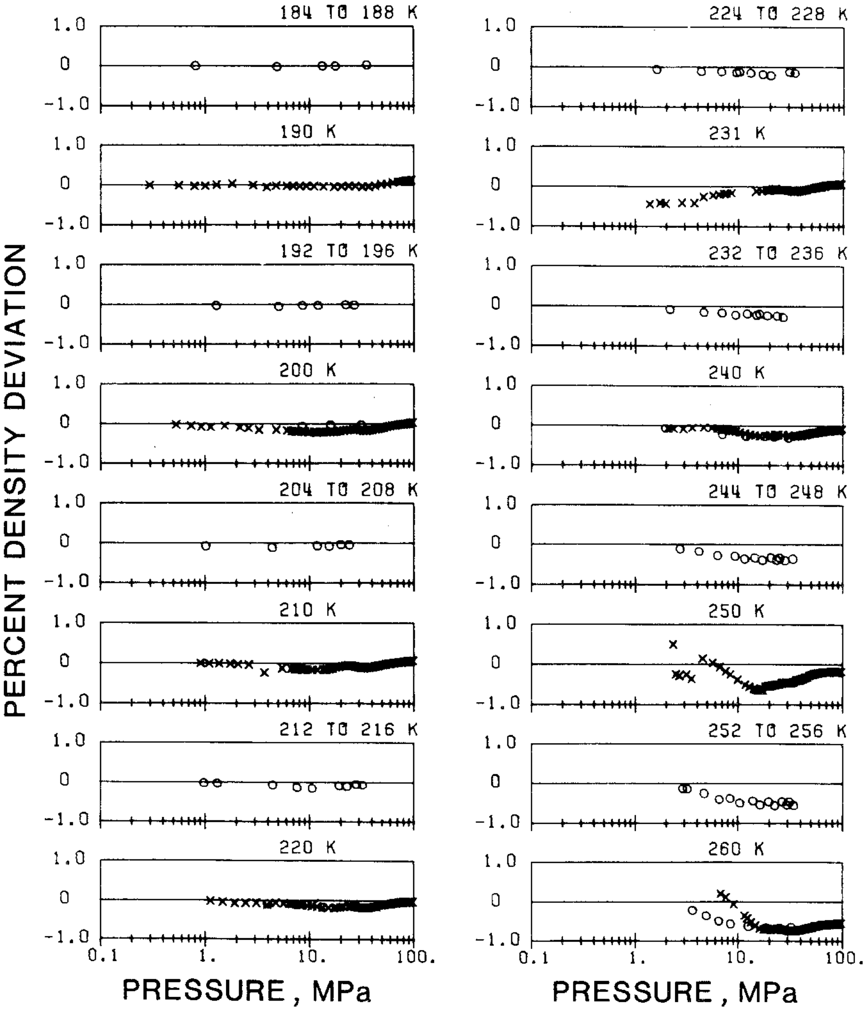

Fig. 1 *(continued)*

The results of the prediction are shown graphically in Figs. 1 and 2. In these figures, the percentage deviation in density is defined as

$$\% \text{ dev} = 100[(\rho_{\text{data}} - \rho_{\text{predicted}})/\rho_{\text{data}}]$$

As can be seen in both of these figures, the prediction of the ethylene

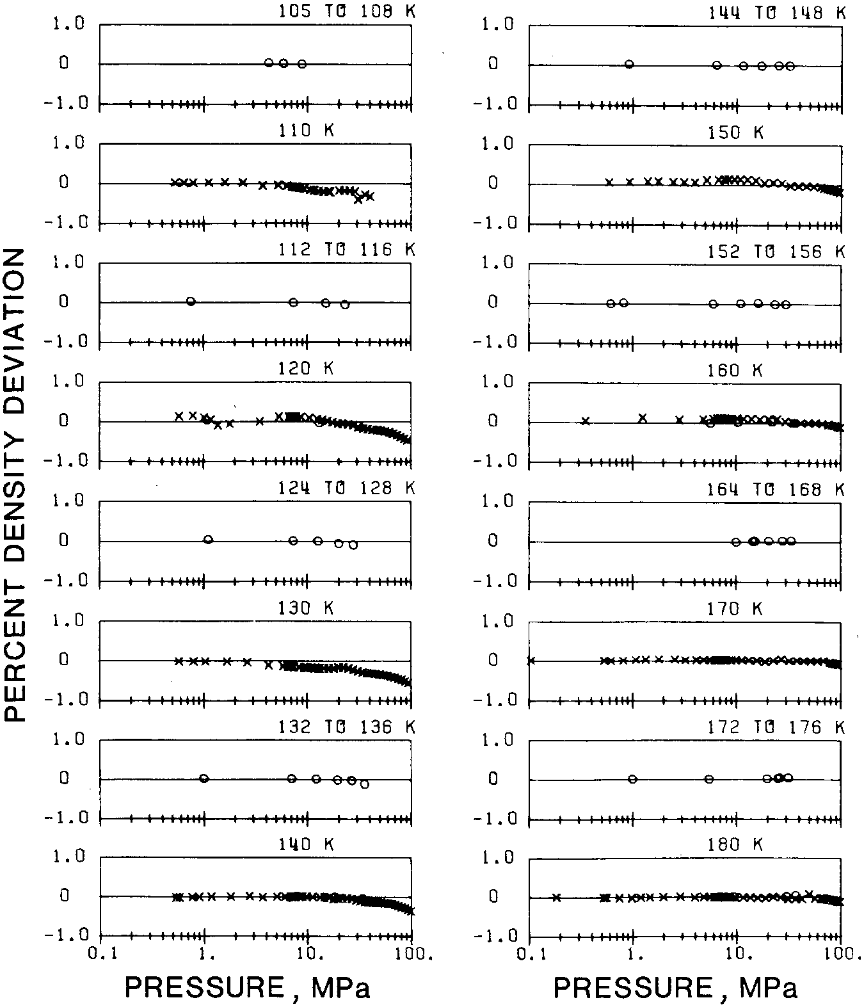

Fig. 2. Comparison of predicted ethylene liquid density using high-density shape factors to experimental data. The reference fluid is nitrogen. The data are from (X) Calado et al. [2] and (O) Straty [3].

density is within ±0.5% of the experimental data for temperatures less than 240 K, which corresponds to a reduced temperature of 0.85. As the pressure increases along an isotherm, the prediction becomes less accurate. This is due to increased dependence of the shape factor upon density at higher pressure states. However, for states below 30 MPa (a reduced pressure of 5.9) most of the predictions are within ±0.2% of the experimental data.

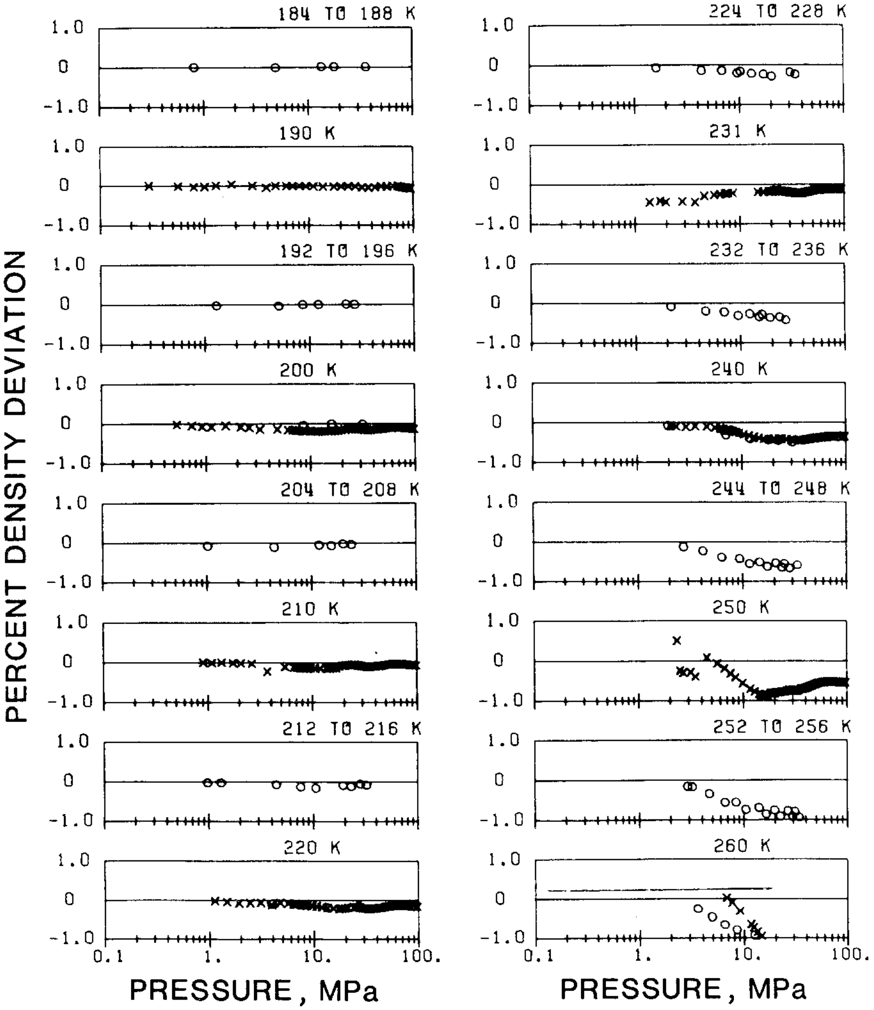

Fig. 2 *(continued)*

4. CONCLUSIONS

With this method of property prediction, molecular similarity between the predicted fluid and the reference fluid is not a strict requirement. However, some fluid combinations may result in an unstable or diverging solution during the iterative calculation of the shape factors. This occurs when the calculation of Z_j or ln ν_j is forced into the two-phase region by θ_{ij} and ψ_{ij} during the course of the iteration.

As with any corresponding-states prediction, the use of accurate equations of state for reference fluids is of paramount importance. The method presented here also requires accurate equations for the vapor pressure, saturated-liquid density, and vapor-phase P–v–T behavior of the fluid being predicted. These requirements may seem to diminish the value of the method. However, this type of information is usually available for the halogenated hydrocarbon refrigerants formulated with the Martin–Hou equation of state.

One of the applications of the method described here is in the development of thermodynamic property formulations. This method may be used to augment already existing experimental data bases. Penoncello [8] used this method to predict high-density single-phase liquid states for dichlorodifluoromethane (refrigerant-12). These predicted data were included with the existing experimental data and an interim thermodynamic property formulation was developed. Additional applications to other fluids are planned in future research.

NOMENCLATURE

P	Pressure
R	Gas constant (8.31434 $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
v	Specific volume
T	Temperature
θ	Temperature shape factor
ψ	Pressure shape factor
ϕ	Volume shape factor
ν	Fugacity coefficient
ρ	Density
σ	Saturation

Subscripts

c	Critical parameter
i	Fluid being predicted
j	Reference fluid
r	Reduced by the critical property

REFERENCES

1. J. W. Leach, Ph.D. dissertation (Rice University, Houston, Tex., 1967).
2. J. C. G. Calado, P. Clancy, A. Heintz, and W. B. Street, *J. Chem. Eng. Data* **27**:376 (1982).
3. G. C. Straty, *J. Chem. Therm.* **12**:709 (1980).
4. R. T Jacobsen, R. B. Stewart, and M. Jahangiri, *J. Phys. Chem. Ref. Data* **15**:735 (1986).
5. R. B. Stewart, R. T Jacobsen, and W. Wagner, Submitted for publication.
6. R. Schmidt and W. Wagner, *Fluid Phase Equil.* **19**:175 (1985).
7. M. Jahangiri, R. T Jacobsen, and R. B. Stewart, *J. Phys. Chem. Ref. Data* **15**:593 (1986).
8. S. G. Penoncello, Ph.D. dissertation (University of Idaho, Moscow, 1986).