Prediction of Some Important Regularities Using a Statistical Mechanical Equation of State

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Four important known regularities for several pure substances have been described using a statistical mechanical equation of state (EOS) derived by Deiters. The equation of state depends on three temperature-independent parameters, which can be obtained from the critical constants. The studied regularities included: (i) near linearity of the reduced isothermal bulk modulus as a function of reduced pressure, (ii) the common bulk modulus point on the isotherms of the reduced bulk modulus versus reduced density, (iii) near linearity of the Zeno contour of reduced temperature against reduced density from the Boyle temperature to the triple point, and (iv) near linearity of the mean density of a saturated liquid and its equilibrium vapor as a function of temperature, called the "law of rectilinear diameter." The results for several fluids have been compared to the available experimental data. The predictions are often satisfactory in the sensitive regions.

1. INTRODUCTION

A precise equation of state (EOS) valid over large intervals of temperature and pressure is a powerful tool for the prediction of thermodynamic properties. As has been pointed out in previous work [1], any sensible EOS is expected to satisfy known regularities. Based on three important regularities (Zeno line, Tait–Murnaghan, and common bulk modulus point), ten van der Waals type EOS were tested in our earlier work for their ability to predict the Zeno contour and the isothermal bulk modulus. As mentioned

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previously, some cubic EOS yield a nearly accurate Zeno line from the Boyle temperature to the triple point, whereas the predictive ability of the bulk modulus regularity obtained from most cubic EOS is usually poor, especially at higher densities.

In this paper, we show that, unlike the cubic van der Waals type EOS, a precise statistical-mechanical EOS, called the Deiters EOS [2, 3], describes the most important regularities. The results show that the Deiters EOS gives better agreement with experiment for both the bulk modulus and Zeno line regularities than the other van der Waals type EOS studied in our previous work. The main objective of this work is therefore to study the performance of the Deiters EOS in predicting the most important regularities. Since the Deiters EOS has a theoretical basis, analysis of the regularities in terms of molecular size and shape is possible. Four of the best known regularities, studied in this work, are the following:

(a) Near linearity of the isothermal bulk modulus (reciprocal compressibility) of a liquid or supercritical fluid as a function of pressure. This regularity was first noticed by P. G. Tait over 100 years ago and is now called the Tait–Murnaghan regularity [4, 5].

(b) Huang and O'Connell have found that isotherms of the bulk modulus as a function of density intersect at a common point [6]; at this density, the bulk modulus is independent of temperature. They checked the existence of this bulk modulus point on over 250 liquids, and used it as the basis of a correlation scheme for the volumetric properties of compressed liquids and liquid mixtures. The location of the common modulus point of course depends on the particular liquid.

(c) Near linearity of a contour in the temperature-density plane along which the compressibility factor $(Z \equiv P/\rho RT)$, equals unity. This $Z = 1$ contour, called the Zeno line, passes from the Boyle temperature at low-density to around the triple point in the liquid region. The properties of the Zeno line were described previously [7].

(d) Approximate linearity of the average of densities of the coexisting liquid and vapor phases in the temperature-density plane. This regularity called the line of rectilinear diameters, and lies in the subcritical region. It has been shown that the situation for the near-critical singularity in the diameter remains ambiguous for normal fluids [8].

2. DEITERS EQUATION OF STATE

An analytical equation of state based on statistical-mechanical perturbation theory was derived by Deiters for a set of spheres interacting through a square-well potential [2, 3]. This equation of state can be written in the reduced form,

$$\frac{P_r}{\rho_r T_r} = \frac{1}{Z_c}\left\{1 + cc_0\frac{4\eta - 2\eta^2}{(1-\eta)^3} - a_r b_r \rho_r \frac{T_{eff}}{T_r}\left[\exp(1/T_{eff}) - 1\right]I(b_r\rho_r)\right\} \quad (1)$$

where $Z_c \equiv P_c V_c / RT_c$ is the critical compressibility factor, $T_r \equiv T/T_c$, $P_r \equiv P/P_c$, and $\rho_r \equiv \rho/\rho_c$ are the reduced temperature, pressure and density of the fluid, respectively, and the characteristic constant $c_0 = 0.6887$ can be regarded as a deviation of the real pair potential from the rigid-core model. The packing fraction η and the effective temperature T_{eff} are defined as

$$\eta = (\pi/6)\,\rho N_A \sigma^3 \quad (2)$$

$$T_{eff} = \frac{\lambda b_r \rho_r + (cT_r/a_r)}{y(b_r\rho_r)} \quad (3)$$

where N_A is Avogadro's constant, $\lambda \equiv -0.06911c$ is a parameter that introduces three-body effects into the EOS, and σ is the molecular diameter, which appears in the square-well potential. The functions $I(b_r\rho_r)$ and $y(b_r\rho_r)$ depend on the single variable $b_r\rho_r$, and their forms are as follows:

$$I(b_r\rho_r) = (\gamma/c)^2 \sum_{n=0}^{5}(n+1)h_n\gamma^n(b_r\rho_r) \quad (4)$$

$$y(b_r\rho_r) = f^2 - c^{-5.5}f(1-f) + (1-0.65/c)(1-f)^2 \quad (5)$$

where

$$h_0 = 7.0794046, \qquad h_1 = 12.08351455, \qquad h_2 = -53.6059$$
$$h_3 = 143.6681, \qquad h_4 = -181.1554682, \qquad h_5 = 78.5739255 \quad (6)$$

$$\gamma = 1 - 0.697816(c-1)^2 \quad (7)$$

and f is the relative free volume, i.e.,

$$f = \exp[cc_0(3\eta^2 - 4\eta)/(1-\eta)^2] \quad (8)$$

Table I. Critical Properties and Deiters Characteristic Parameters for Several Substances (Values of critical constants are taken from the reported references in the last column)

Substance	T_c (K)	P_c (MPa)	ρ_c (mol·L^{-1})	Z_c	a_r	b_r	c	Ref.
Ne	44.42	26.54	23.88	0.303	0.6855	0.2223	1.000	20
Ar	150.69	48.63	13.25	0.289	0.6883	0.2205	1.000	21
Kr	209.39	54.96	10.87	0.290	0.6872	0.2237	1.000	22
Xe	289.74	58.34	8.37	0.290	0.6868	0.2124	1.000	23
CH_4	190.53	45.98	10.16	0.288	0.6876	0.2243	1.000	21
C_2H_6	305.34	48.71	6.87	0.280	0.8980	0.2181	1.121	21
C_3H_8	369.85	42.48	5.00	0.276	1.0218	0.2149	1.176	21
$n\text{-}C_4H_{10}$	425.16	37.96	3.92	0.274	1.1158	0.2161	1.212	16
N_2	126.19	3.395	11.21	0.289	0.6875	0.2250	1.000	21
O_2	154.58	5.043	13.63	0.288	0.6870	0.2269	1.000	24
F_2	144.42	5.173	15.603	0.276	0.6855	0.2309	1.000	17
CO_2	304.13	7.377	10.625	0.275	1.0962	0.2171	1.205	21

It has been shown that the Deiters EOS gives good predictions for vapor-liquid equilibrium (VLE) and PVT properties for nonpolar and weakly polar substances [9]. Equation (1) has three adjustable parameters, the reduced characteristic temperature a_r, the reduced covolume b_r, and a correction factor c for the number density, which can be interpreted as a shape parameter, with $c = 1$ for spherical molecules. Baonza and collaborators [9] have suggested a general procedure to obtain these three parameters from a knowledge of the critical variables. The values of Deiters characteristic parameters for several substances are given in Table I.

3. REGULARITIES IN DENSE FLUIDS

3.1. Linearity of B_T Versus P

The reduced bulk modulus B_T, which is a mechanical property, can be written as

$$B_T = \frac{Z_c}{T_r}\left(\frac{\partial P_r}{\partial \rho_r}\right)_{T_r} \tag{9}$$

The reduced bulk modulus of a dense fluid has been empirically found to be linear in the reduced pressure for each isotherm, i.e.,

$$B_T = B_{0,T} + B'_{0,T} P_r \tag{10}$$

where $B_{0,T}$ and $B'_{0,T}$ are temperature-dependent parameters. Such linearity is known as the Tait–Murnaghan regularity. This regularity is satisfactorily reproduced for a number of successful empirical equations of state, such as the Peng–Robinson, Soave–Redlich–Kwong, and modified Patel–Teja equations of state [1].

3.2. Common Bulk-Modulus Point

Another regularity in the behavior of the reduced bulk modulus has been reported by Huang and O'Connell [6], which states that the isotherms of B_T versus ρ_r intersected at a common point, called the common bulk-modulus point. The value of B_T is independent of temperature at this density, i.e.,

$$\left(\frac{\partial B_T}{\partial T_r}\right)_{\rho_{0,r}} = 0 \tag{11}$$

where $\rho_{0,r}$ is the reduced density of the fluid at the common bulk-modulus point. This regularity lies in the liquid region, and the location of the common modulus point of course depends on the particular liquid. As has pointed out in our previous work [1], most of the cubic van der Waals type EOS do not show a common intersection point, but in this work we show that the Deiters EOS predicts a (nearly) common modulus point, consistent with the empirical findings of Huang and O'Connell.

3.3. Zeno Contour

For a wide range of normal fluids, including nonpolar and weakly polar fluids, a contour in the temperature-density plane along which the compressibility factor equals unity, known as the Zeno line, has been empirically observed to be nearly linear from the Boyle temperature at low density to around the triple point in the liquid region. The regularity provides a significant constraint for testing or improving volumetric equations of state. The properties of the Zeno contour are described by Ben-Amotz and Herschbach [7]. The Zeno condition can be written as

$$T_r = w_1 - w_2 \rho_r \tag{12}$$

where w_1 and $-w_2$ are the intercept and slope of the Zeno line, respectively. At the low-density limit, with $\rho_r \to 0$, the intercept of the Zeno line in a T_r–ρ_r plane is specified by the reduced Boyle temperature.

The Zeno line phenomenon has been found to extend to a wide range of fluids well beyond the realm of standard corresponding states, with strong correlations to the line of rectilinear diameters from subcritical to supercritical conditions [10].

3.4. Rectilinear Diameter

The average of the densities of the coexisting liquid and vapor phases, called the "diameter," is defined as
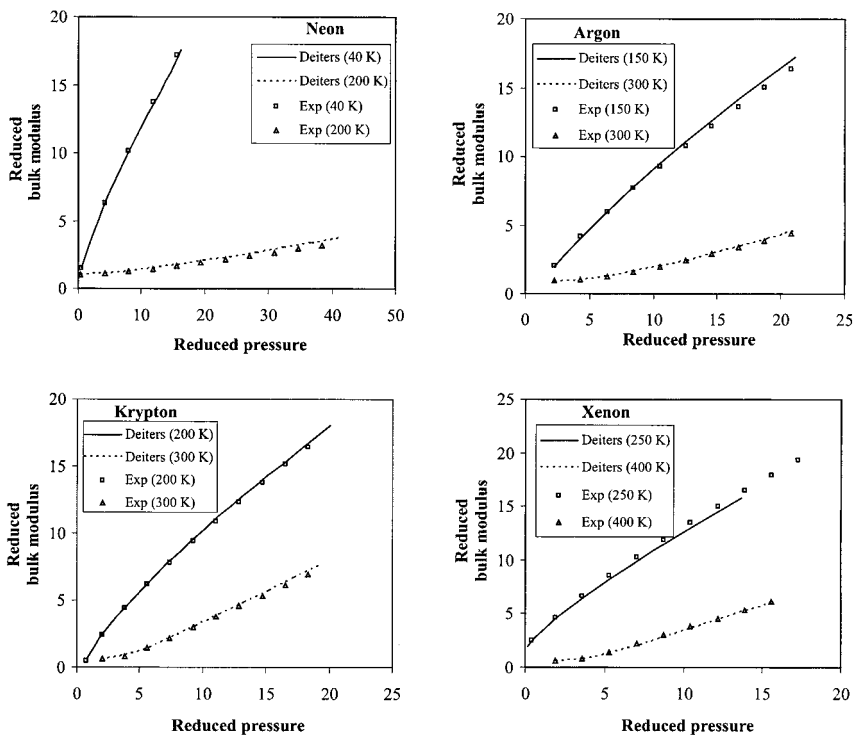
$$\rho_d \equiv \frac{\rho_l + \rho_v}{2} \tag{13}$$

Fig. 1. Comparison between the experimental and predicted Tait–Murnaghan regularity for noble gases. Predictions are represented by continuous lines and the experimental data by symbols. Experimental values are determined from Eq. (15). The heat-capacity ratio and the speed-of-sound data are taken from Refs. 12 to 15.

where ρ_l and ρ_v are the saturated density of the liquid and vapor, respectively. Empirically, it was shown that the reduced diameter $\rho_{d,r} \equiv \rho_d/\rho_c$ is a linear function of the reduced temperature T_r in the temperature-density plane [8],

$$\rho_{d,r} = A_1 - A_2 T_r \qquad (14)$$

where A_1 and $-A_2$ are the intercept and slope of the rectilinear diameter, respectively.

This regularity, called "the law of rectilinear diameters," lies in the subcritical region, and it has been shown that it breaks down in the vicinity of the critical point [10].
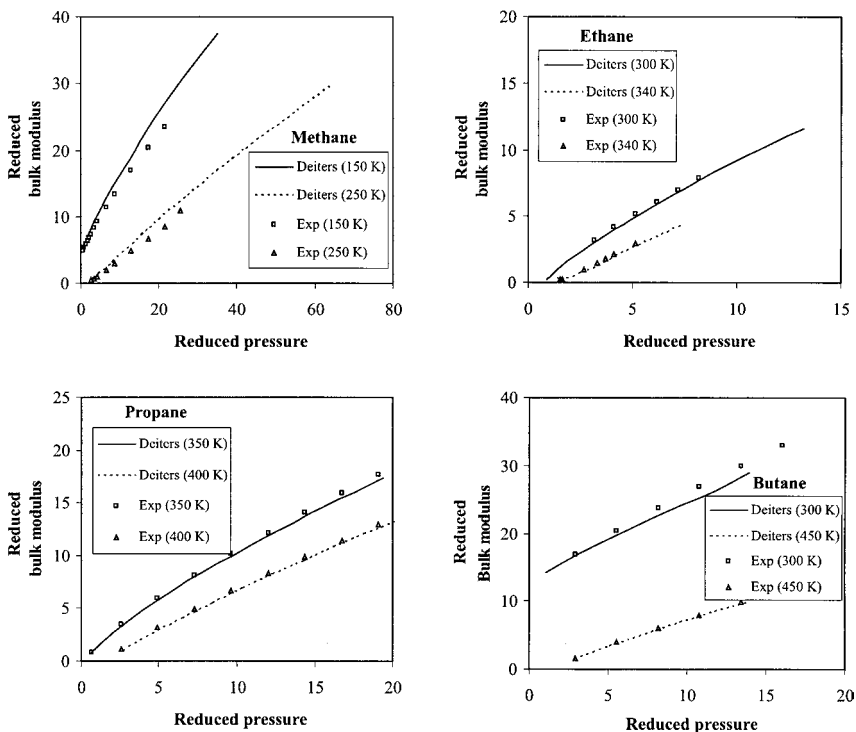
Fig. 2. Same as Fig. 1 for CH_4, C_2H_6, C_3H_8, and n-C_4H_{10}. Experimental values are determined from Eq. (15). The heat-capacity ratio and speed-of-sound data are taken from Ref. 16.

4. RESULTS AND DISCUSSION

The Deiters EOS has been used to predict the $P\rho T$ equilibrium surface over a large pressure range and the second virial coefficients for several pure substances, such as noble gases, n-alkanes, and other selected substances such as O_2, N_2, F_2, and CO_2 [9]. It was shown that the predictions are very satisfactory, being within the experimental uncertainties in most cases. The equation was also shown to give good accuracy for the Joule–Thomson inversion behavior [11].

In this work, we calculate the bulk modulus from Eq. (9) at each reduced temperature and pressure by initially solving Eq. (1) for any chosen ρ_r and T_r. Figures 1 to 3 show the calculated isothermal reduced bulk modulus B_T as a function of reduced pressure for two temperatures and for three sets of substances including the noble gases, some hydrocarbons and some other selected substances such as O_2, N_2, F_2, and CO_2.
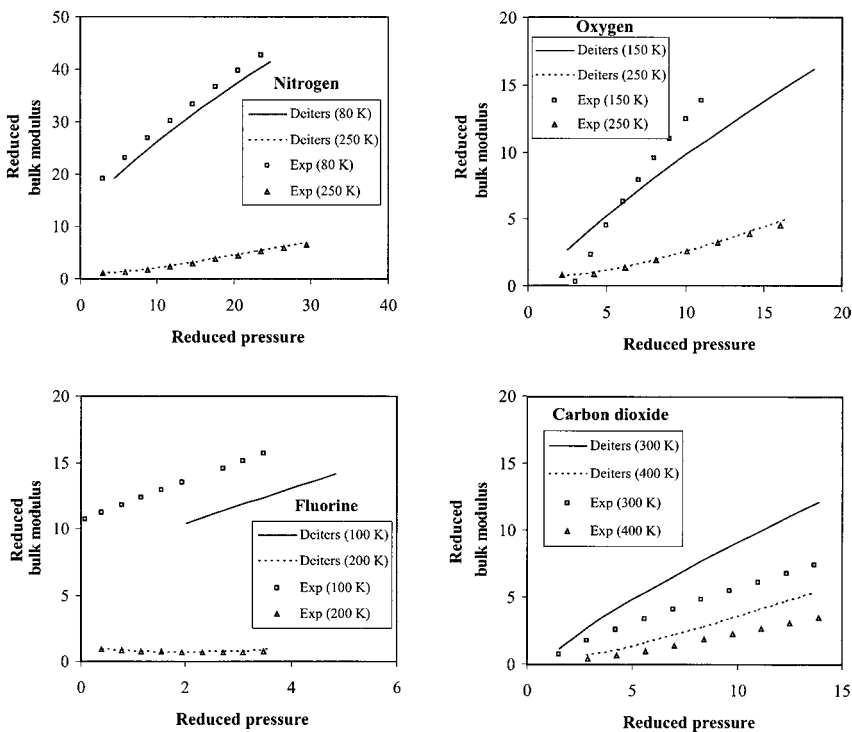

Fig. 3. Same as Fig. 1 for N_2, O_2, F_2, and CO_2. Experimental values are determined from Eq. (15). The heat-capacity ratio and speed-of-sound data are taken from Refs. 17 to 19.

Comparisons are made with experimental data [12–20], where the predictions are represented by continuous lines and the experimental data by symbols. As shown, at high pressures an approximate linear behavior of the Tait–Murnaghan regularity is obtained for all selected substances. The calculated isothermal bulk modulus as a function of reduced pressure is consistent with the experimental values for noble gases, n-alkanes, and N_2 in both the liquid and supercritical regions, whereas for O_2 and F_2, the Deiters EOS shows good predictions at supercritical conditions, but it shows some deviations in the liquid region. Moreover, we observe that the agreement between the predictions and the experimental values for CO_2 is relatively poor in both the liquid and supercritical regions. In our present work, the experimental isothermal bulk modulus of fluids is determined from the heat-capacity ratio and speed-of-sound data described in the following manner.
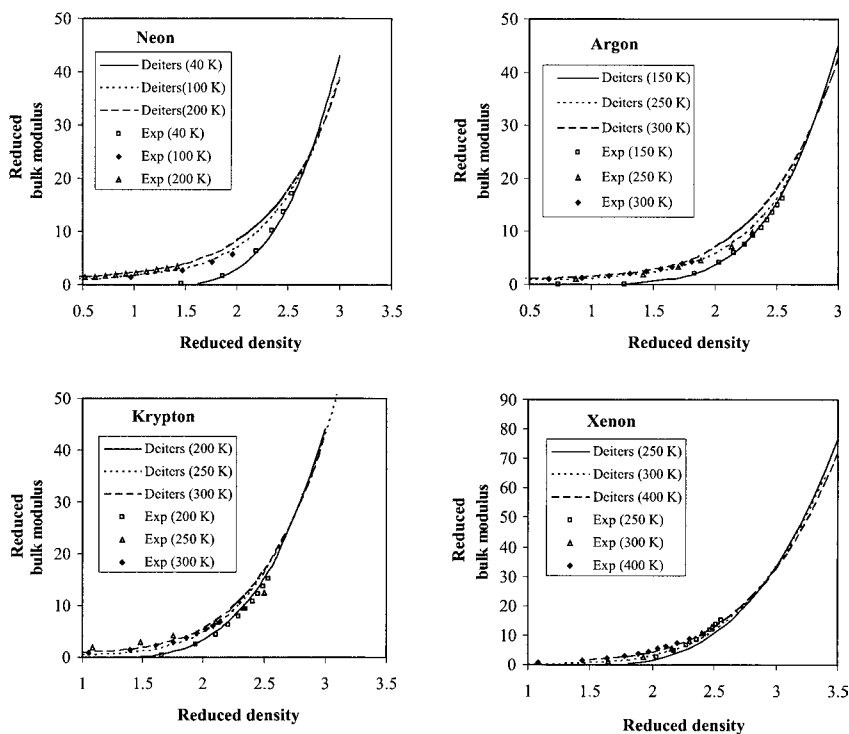

Fig. 4. Comparison between the experimental and predicted isothermal bulk modulus as a function of reduced density for noble gases. Predictions are represented by continuous lines and the experimental data by symbols. Experimental values are determined from Eq. (15). The heat-capacity ratio and speed-of-sound data are taken from Refs. 12 to 15.

The propagation of sonic waves is nearly isentropic, so by using Eq. (9) we can calculate the isentropic sound speed v_s for real systems as

$$v_s = \left[\frac{\gamma RT}{M} \left(\frac{\partial P_r}{\partial \rho_r} \right)_{T_r} \right]^{1/2} = \left[\frac{\gamma RT}{M} B_T \right]^{1/2} \tag{15}$$

in which R is the universal gas constant, M is the molecular weight, and γ is the heat-capacity ratio, $\gamma \equiv C_P / C_V$. Therefore, the experimental values of the isothermal bulk modulus can be obtained from experimental data of the speed of sound and the heat-capacity ratio of the system.

Figures 4 to 6 show the calculated isothermal reduced bulk modulus B_T as a function of reduced density ρ_r for three temperatures for three sets of substances in comparison with experimental data. As can be seen, the isothermal bulk-modulus for Ne, Ar, and Kr is well matched by the Deiters EOS for both low- and high-density regions, whereas for Xe it performs
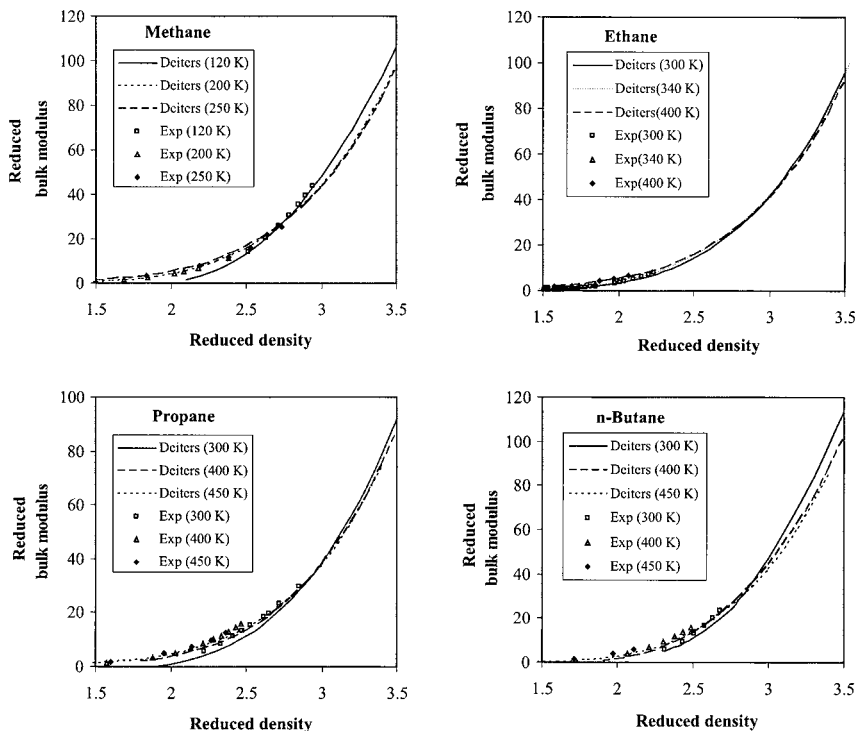

Fig. 5. Same as Fig. 4 for CH_4, C_2H_6, C_3H_8, and n-C_4H_{10}. Experimental values are determined from Eq. (15). The heat-capacity ratio and speed-of-sound data are taken from Ref. 16.
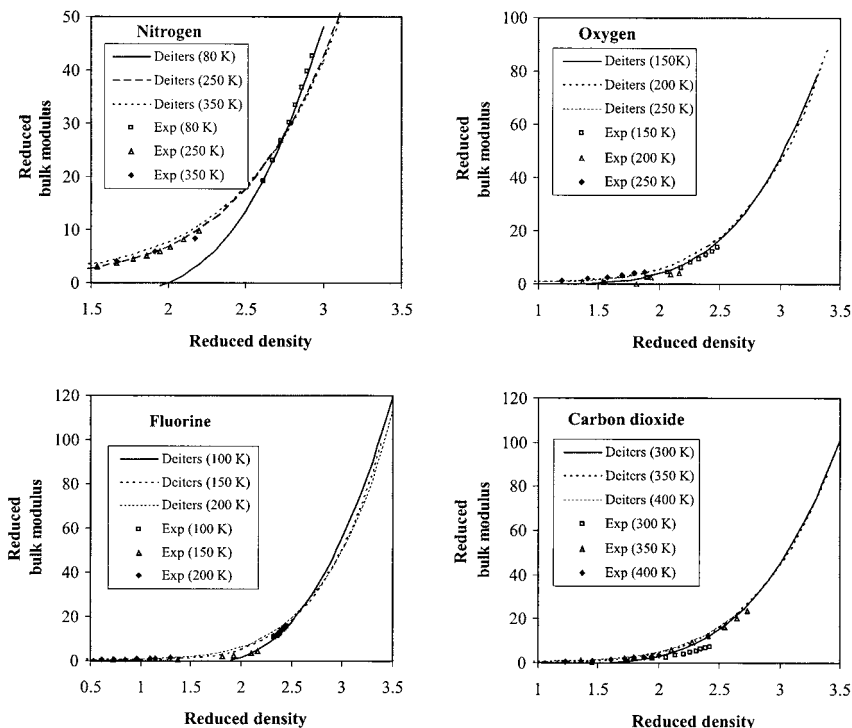
Fig. 6. Same as Fig. 4 for N_2, O_2, F_2, and CO_2. Experimental values are determined from Eq. (15). The heat-capacity ratio and speed-of-sound data are taken from Refs. 17 to 19.

well in the supercritical region. For the *n*-alkanes CH_4, C_2H_6, C_3H_8, and n-C_4H_{10}, the results are within the experimental uncertainties, except for n-C_4H_{10} at higher densities. Figure 6 shows that the predictions for N_2, O_2, and F_2 are in general very satisfactory, even at higher densities; however, speed-of-sound data for fluorine are rather scarce in the literature. Additionally, a discrepancy is found on the liquid branch of CO_2 at $\rho_r > 2.2$. As can be seen from Figs. 4 to 6, the Deiters EOS predicts this intersection point, while our previous work showed that the cubic van der Waals type equations of state are not capable of predicting the common intersection point. The predicted common intersection points $\rho_{0,r}$ for selected substances of this work are given in Table II.

Figure 7 shows the calculated Zeno contours (T_r–ρ_r plane) of several fluids using the Deiters EOS as compared to the experimental Zeno line, where the calculations are represented by continuous lines and the experimental data by symbols. As may be observed, in the case of noble gases, the results are extremely good. For hydrocarbons, the calculated Zeno

Table II. Predicted Common Intersection Point

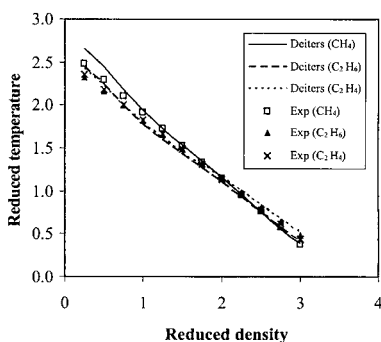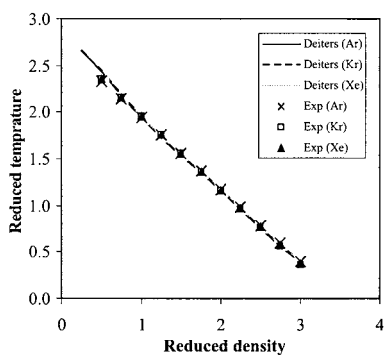| Substance	$\rho_{0,r}$	$B_T(\rho_{0,r})$
Ne	2.72	24.7
Ar	2.73	24.8
Kr	2.72	25.6
Xe	2.87	25.9
CH_4	2.74	27.0
C_2H_6	2.77	27.5
C_3H_8	2.86	31.3
$n\text{-}C_4H_{10}$	2.89	33.9
N_2	2.80	29.4
O_2	2.66	24.6
F_2	2.65	26.4
CO_2	2.80	30.6
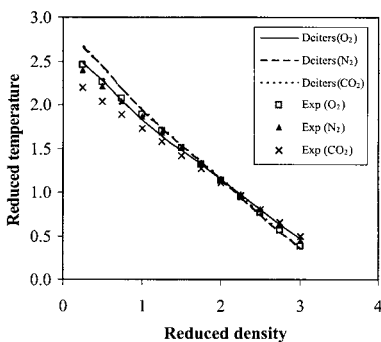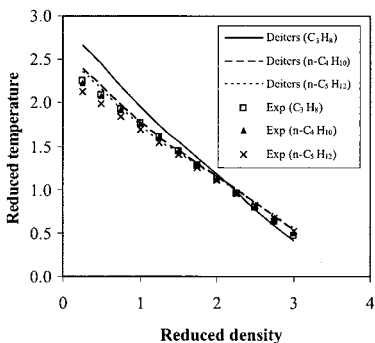
Fig. 7. Comparison between the experimental and predicted Zeno contours of several substances. Predictions are represented by continuous lines and the experimental data by symbols. Experimental data are taken from Ref. 10.
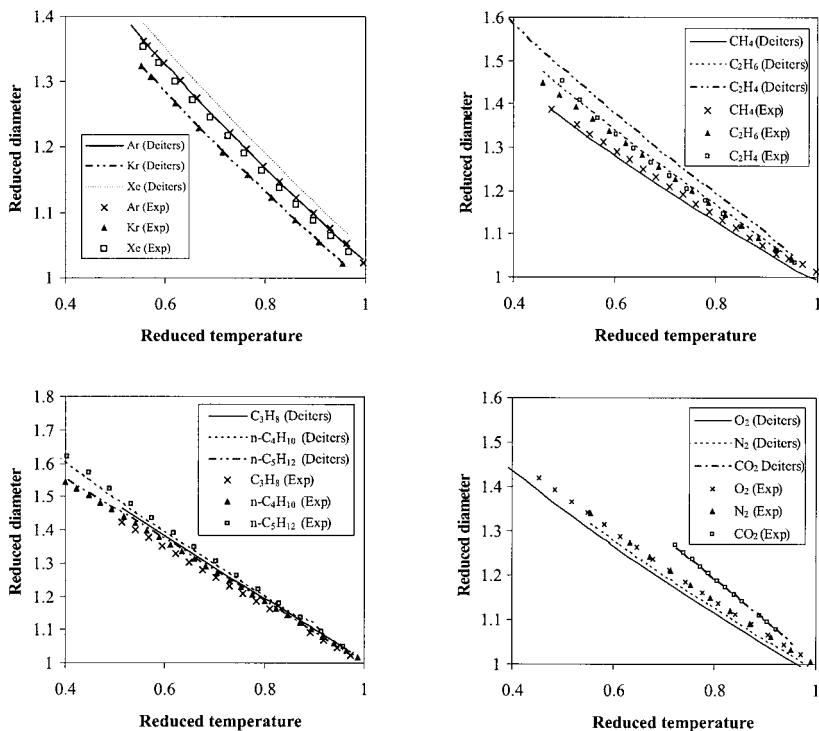
Fig. 8. Comparison between the experimental and predicted "reduced diameters" as a function of reduced temperature of several substances. Predictions are represented by continuous lines and the experimental data by symbols.

contours compare well, except for C_3H_8 for which the slope is larger than the corresponding experimental value. Moreover, the predicted Zeno contour for O_2 is well matched by the Deiters EOS, while predictions for N_2 and CO_2 show some deviations in the low-density regions.

Figure 8 shows the predicted "reduced diameters" ($\rho_{d,r}$) as a function of reduced temperature T_r of several selected substances as compared to experimental data. As shown in Fig. 8, the contour in the $\rho_{d,r}-T_r$ plane is exactly linear, but the slope or intercept of some substances are slightly different from the corresponding experimental values.

5. CONCLUSION

In this work, we have worked with a statistical equation of state, called the Deiters EOS, to test for four important regularities: (i) Tait–Murnaghan regularity, (ii) common bulk-modulus intersection point,

(iii) linearity of the Zeno contour, and (iv) law of rectilinear diameters. The Tait–Murnaghan regularity of the isothermal bulk modulus as a function of reduced pressure exists for both subcritical and supercritical fluids over a wide pressure range. The regularity of the isothermal bulk modulus as a function of density retains its common intersection even in the compressed liquid. Moreover, the Zeno line lies largely in the supercritical region, whereas the line of rectilinear diameters of course lies in the subcritical region.

These results show that the Deiters EOS can be used for good predictions of the Tait–Murnaghan regularity as well as the common intersection points for most selected substances. The results also demonstrate that the Deiters EOS yields a nearly accurate and straight Zeno line for most substances. We have also observed that the "law of rectilinear diameter" is satisfied by the Deiters EOS for all selected substances in this work.

ACKNOWLEDGMENT

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