

# Complexity of Density Dependencies of Thermal and Internal Pressure Compared to That of Total Pressure

Sayyed Hashem Sajjadi and Gholamabbas Parsafar\*

Department of Chemistry, Sharif University of Technology, Tehran, 11365-9516, Iran

**ABSTRACT:** A simple equation of state (EoS) has recently been introduced (*J. Phys. Chem. B* **2009**, *113*, 11977–11987) as  $(Z - 1)v^2 = e + f/\rho + g\rho^2$ , where  $Z \equiv pv/RT$  is the compressibility factor,  $v = 1/\rho$  is molar volume, and  $e$ ,  $f$ , and  $g$  are temperature dependent parameters. This EoS has been found to be accurate for all types of nano and bulk solids and bulk fluids, in the entire temperature and pressure ranges for which experimental data are reported, except for the isotherms within  $1 \leq T_r = T/T_c \leq 1.1$  for the spherical and near spherical species and for a wider temperature range for the cylindrical molecules. The aim of this work is to investigate the validity of a three-term expression similar to the mentioned EoS for both thermal and internal contributions to the compressibility factor, separately. Such investigation shows that although the total pressure obeys the EoS well, neither its thermal nor its internal contributions follow a similar three-term expression. Therefore, there are some terms in the individual pressure contributions, which cancel each other out in the total pressure, which makes the EoS so simple. However, we have found that there is one extra term in each contribution which does not cancel out in the total pressure, for the isotherms within the critical region. Such a term significantly improves the isotherms near the critical isotherm, compared to the original EoS. The added term to the pressure components also improves both thermal and internal pressures in the entire temperature range. The results of this work show that, although semiempirical EoSs such as van der Waals, Redlich–Kwong, and EoS-III are fairly accurate in describing the pressure behavior of fluids, except in the critical region, they may show a remarkable deviation for the thermal and internal pressures. Finally, the obtained expression for the internal compressibility factor along with the EoS is used to derive internal energy, enthalpy, entropy, heat capacity at constant volume, and constant pressure each as a quadric function in density, for each isotherm, out of the critical region.

## 1. INTRODUCTION

The thermal pressure coefficient,  $(\partial p/\partial T)_v$ , is one of the most important fundamental properties which is closely related to various properties, such as the entropy of melting, isothermal compressibility, and isobaric expansibility.<sup>1</sup> Thus, the study of the thermal pressure coefficient could provide a useful basis for understanding the nature of fluids and solids. On the other hand, the cohesive forces which are due to the forces of attraction and repulsion among fluid molecules, holding them together and creating pressure within the fluid which, are called the internal pressure. Internal pressure,  $-(\partial E/\partial v)_T$  where  $E$  is the internal energy, a fundamental fluid property, is closely related to different properties of fluids such as ultrasonic velocity, free volume, viscosity, surface tension, solubility parameter, and latent heat of vaporization in the liquid phase.<sup>2</sup>

Obtaining physical properties of a substance via theoretical methods such as statistical thermodynamics is difficult because of the complex nature of intermolecular interactions. Hence, experimental methods have attracted much attention. Remarkable experimental data,<sup>3–9</sup> simple regularities, and theoretical results have been reported in the literature.<sup>10–18</sup>

Moeini<sup>15</sup> reported that the quantity  $[(\partial E/\partial v)_T/\rho RT]v^2$  is linear with  $\rho^2$  by using the linear isotherm regularity (LIR) equation of state (EoS).<sup>19</sup> This regularity provides a relation between internal pressure and volume. Goharshadi et al.<sup>2</sup> computed the internal pressure for different liquids using a statistical mechanical equation of state and investigated a relation between the internal pressure and external (thermal) pressure. Siepmann et al.<sup>16</sup> found a parabola pressure function from simulations of the internal pressure for various

compounds and provided an additional structural information (pressure dependency of the radial distribution function and hydrogen bonding). Zeng et al.<sup>17</sup> proposed an empirical regularity for dense fluids, which was the thermal pressure coefficient is a near-parabola function of pressure. This regularity was tested with experimental data and the statistical results showed its accuracy.

There are three types of EoS: empirical, theoretical, and semiempirical.<sup>20</sup> Empirical EoSs contain a large number of parameters whose values depend merely on the material. Usually, these parameters have no physical meaning and simply are adjustable parameters. These EoSs are suitable for one or a small group of materials, and the obtained thermodynamic properties from such EoSs are very accurate in the range of fitting pressure and temperature but, for other materials or outside the range, are not valid. Some famous empirical EoSs are the Tait,<sup>21</sup> Benedict–Webb–Rubin,<sup>22</sup> and Helmholtz function forms.<sup>23</sup> Theoretical EoSs have temperature dependent parameters with a physical meaning. Due to theoretical limitations, such EoSs are not usually as accurate as the previous ones, but they are able to calculate thermodynamic properties outside the defined range. Theoretical EoSs are generally based on statistical mechanics and are obtained using the concept of the radial distribution function or perturbation

**Received:** February 13, 2013

**Revised:** May 8, 2013

**Accepted:** May 16, 2013

theory. Song and Mason<sup>24</sup> introduced an analytical-theoretical EoS using the concepts of the statistical mechanics for the molecular liquids. Unlike the empirical equations, semi-empirical EoSs require little experimental data. In fact, this type of EoSs has a combination of characteristics of both theoretical and empirical equations. The van der Waals (vdW),<sup>25</sup> Redlich–Kwong (RK),<sup>26</sup> and LIR<sup>19</sup> EoSs are a few semiempirical EoSs among many.

Thermodynamic properties of fluids at high pressures are of much interest in a variety of chemical industrial processes, notably for separation processes in natural-gas and gas condensates production, supercritical extraction, and fractionation of petroleum.<sup>27,28</sup> Some of the separation processes encounter the critical conditions. The way mean-field equations such as the van der Waals and Redlich–Kwong EoSs incorporate molecular attraction and repulsion implies neglecting fluctuations. This neglecting of both local and long-range structure is an impediment to characterizing liquids and supercritical fluids. In particular, mean-field theory is unable to describe the critical behavior properly.<sup>29</sup> The asymptotic nature of singular behavior of fluids near the critical point is described in terms of the scaling laws with the universal critical exponents and universal scaling functions.<sup>30,31</sup> The region of application of these functions is quite small;<sup>32</sup> in other words, the influence of these functions is observed only in a very small range of temperature and density near the critical point. It is also observed that the critical fluctuations affect the thermodynamic properties over wide ranges of temperature and density.<sup>33</sup>

Many researchers have proposed various empirical<sup>34,35</sup> and theoretical<sup>36–44</sup> EoSs to predict the behavior of fluids near the critical region. Lee et al.,<sup>36</sup> Feyzi et al.,<sup>37</sup> and Wyczalkowska et al.<sup>38</sup> developed a crossover cubic model near and far from the critical region using the Patel–Teja (PT),<sup>45</sup> Peng–Robinson (CPR),<sup>46</sup> and vdW EoSs, respectively. Jiang and Prausnitz<sup>39</sup> developed a crossover equation of state upon incorporation of contributions from long-wavelength density fluctuations by a renormalization-group theory (EoS<sub>SCF</sub> + RG) for describing thermodynamic properties of chain fluids. However, all mentioned models show a deviation at high densities or pressures.

Recently, an accurate equation of state (EoS-III),<sup>47</sup> based on an effective near-neighbor pair interaction of an extended Lennard-Jones (12, 6, 3) type, was proposed by Parsafar and co-workers. The equation of state gives a good description for all types of fluids, quantum light molecules,<sup>48</sup> nonpolar (including long-chain hydrocarbons), polar, hydrogen-bonded, an ionic liquid model, and metallic, at temperatures ranging from the triple point to the highest temperature for which there is experimental data. For fluids, there appears to be no upper density limitation on the equation of state. The lower density limit for isotherms near the critical temperature is the critical density. For solids, the equation of state is very accurate for all types considered, including covalent, molecular, metallic, ionic, and nanosystems.<sup>49</sup> Recently, the validity of EoS-III was evaluated for confined water in the carbon nanotubes with different diameters.<sup>50</sup> The mathematical expression for EoS-III is

$$(Z - 1)v^2 = e + \frac{f}{\rho} + g\rho^2 \quad (1)$$

or

$$(Z_{\text{th}} + Z_{\text{in}}) - 1 = f\rho + e\rho^2 + g\rho^4 \quad (2)$$

where  $Z = p/\rho RT$  is the compressibility factor,  $p$  and  $\rho$  stand for pressure and molar density, respectively,  $T$  is temperature, and  $e, f,$  and  $g$  are the temperature dependent coefficients of the equation of state. The  $Z_{\text{th}}$  and  $Z_{\text{in}}$  are the thermal and internal contributions of pressure in the compressibility factor, respectively.

The aim of this work is to investigate the validity of a three-term expression similar to eq 1 (given by eqs 3a and 3b) for both thermal and internal contributions to the compressibility factor, separately. We shall examine the validity by three approaches: (i) using an accurate empirical EoS to calculate thermal and internal pressure, (ii) using the modified hard sphere EoS for calculation of the thermal pressure of the real fluids, and (iii) using a quite accurate<sup>51</sup> two-parameter RK-EoS to find appropriate expressions for both thermal and internal pressures. Then, the RK-EoS will be used to modify EoS-III for the critical region. The predictive power of the modified EoS-III will be investigated for some fluids within the critical region. Finally, we shall derive and present analytical expressions for the internal energy, enthalpy, entropy, and heat capacity, based on the obtained internal pressure and using EoS-III.

## 2. POSSIBILITY OF PRESENTING THERMAL AND INTERNAL PRESSURES BY A SIMPLE THREE-TERM EXPRESSION IN DENSITY

One may simply assume that in order to have EoS-III, both thermal and internal pressures have similar density dependencies, as

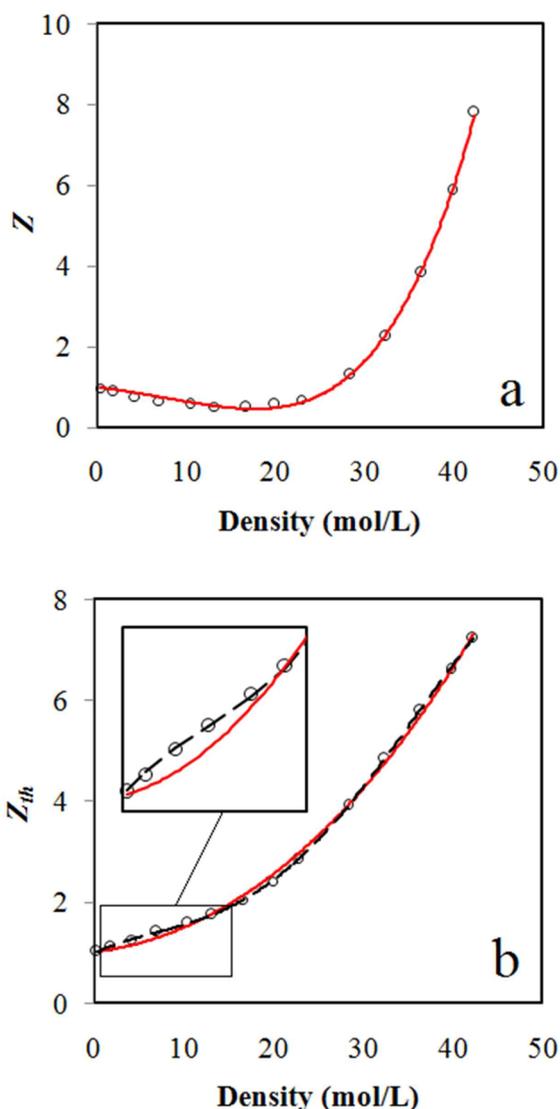
$$Z_{\text{th}} = \frac{p_{\text{th}}}{\rho RT} = 1 + e_{\text{th}}\rho^2 + f_{\text{th}}\rho + g_{\text{th}}\rho^4 \quad (3a)$$

$$Z_{\text{in}} = \frac{p_{\text{in}}}{\rho RT} = e_{\text{in}}\rho^2 + f_{\text{in}}\rho + g_{\text{in}}\rho^4 \quad (3b)$$

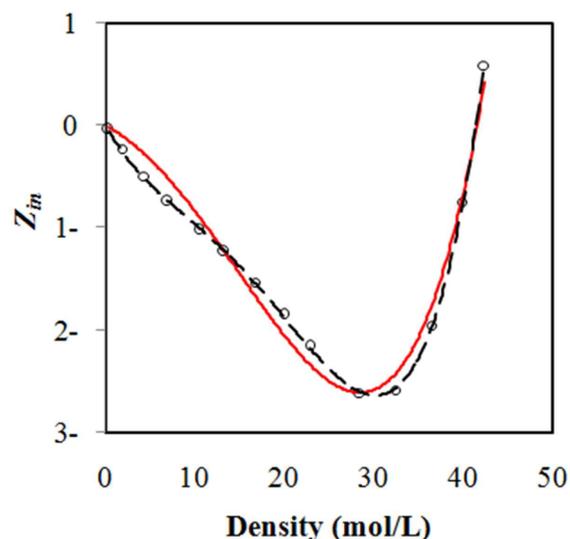
where  $p_{\text{th}}$  and  $p_{\text{in}}$  are the thermal and internal pressures respectively, and  $e_{\text{th}}, f_{\text{th}},$  and  $g_{\text{th}}$  are temperature dependent coefficients of  $Z_{\text{th}}$  and  $e_{\text{in}}, f_{\text{in}},$  and  $g_{\text{in}}$  are those for  $Z_{\text{in}}$ . Note that for  $\rho \rightarrow 0$ , a fluid behaves ideally,  $Z_{\text{th}} = 1$  and  $Z_{\text{in}} = 0$ , because of the fact that there is no interaction among molecules in the ideal state. To examine such an assumption, we have used the empirical EoS of argon (Ar),<sup>52</sup> to calculate its thermal pressure. This equation of state contains 41 coefficients. For the density, the estimated uncertainty of this EoS is less than  $\pm 0.02\%$  for pressures up to 12 MPa and temperatures up to 340 K, with the exception of the critical region and less than  $\pm 0.03\%$  for pressures up to 30 MPa and temperatures within 235–520 K. This EoS shows a reasonable extrapolation behavior up to very high pressures and temperatures. The thermal pressure of Ar may be calculated simply by taking the differentiation of  $p$  with respect to  $T$  using its empirical EoS and multiply the result by  $T$  for each isotherm. The internal pressure is the difference of the total pressure and thermal pressure ( $p - p_{\text{th}}$ ). We have calculated the pressure components for 145 and 200 K isotherms of Ar. Some results are given in Table 1. Then eqs 3a and 3b have been fitted onto the calculated thermal and internal compressibility factor for 180 K isotherm of Ar shown in Figures 1 and 2 with the solid curves, respectively. As shown in these figures, even though EoS-III well fits onto the points, neither eqs 3a nor 3b fit onto the thermal and internal contributions, respectively. The coefficient of determination ( $R^2$ ) for the former fit is 0.99941, while for the latter fits it is

**Table 1.** Calculated Pressure Components for 145 and 200 K Isotherms of Ar Using the Empirical EoS<sup>52</sup>

T (K)	$\rho$ (mol/L)	$p_{\text{tot}}$ (MPa)	$p_{\text{th}}$ (MPa)	$p_{\text{in}}$ (MPa)
145	22.82	5.000	74.15	-69.15
	26.89	15.00	121.9	-106.9
	31.00	45.00	180.7	-135.7
	34.02	90.00	231.6	-141.6
	38.63	220.0	325.4	-105.4
200	7.359	9.000	17.26	-8.260
	31.38	116.5	232.8	-116.3
	38.00	306.5	375.2	-68.70
	40.97	458.5	449.4	9.100
	42.69	572.5	495.1	77.40

**Figure 1.** Fitting (a) EoS-III onto the calculated compressibility factor and (b) eq 3a onto the calculated thermal compressibility factor for the 180 K isotherm of argon, using the empirical EoS (solid curves). Also, the fitting of eq 13 is shown by the dash curve.

0.99845 and 0.97976, respectively (see Table 2). The results for similar fittings (including  $R^2$  and the average absolute percent deviation of pressure (AAD%)) for one subcritical and seven supercritical isotherms of Ar are summarized in Table 2. On the basis of results given in Table 2, one may notice that the fitting

**Figure 2.** Same as Figure 1 except for the internal pressure which is fitted by eqs 3b and 16.**Table 2.** Coefficient of determination ( $R^2$ ) for the Fitting of Equations 2, 3a, and 3b onto the Calculated Values of  $Z$ ,  $Z_{\text{th}}$ , and  $Z_{\text{in}}$ , Respectively, Obtained from the Empirical EoS of Ar for the Given Isotherms<sup>a</sup>

T (K)	$\Delta p$ (MPa)	$R^2$ (AAD%) <sup>b</sup>		
		$z$	$Z_{\text{th}}$	$Z_{\text{in}}$
argon				
145	3–290	0.99990	0.99922	0.99824
		(3.4512)	(0.96860)	(0.92540)
151	0–325	0.99813	0.99576	0.94501
		(14.342)	(5.6419)	(18.212)
160	0–375	0.99896	0.99795	0.96732
		(8.2460)	(3.8111)	(17.616)
165	0–405	0.99903	0.99802	0.96713
		(7.8174)	(3.9783)	(22.329)
180	0–495	0.99941	0.99845	0.97976
		(5.6540)	(3.2780)	(22.552)
200	0–635	0.99971	0.99908	0.98830
		(3.6164)	(2.5787)	(16.833)
300	5–1000	0.99996	0.99964	0.99826
		(0.92580)	(1.2632)	(11.243)
400	5–1000	0.99999	0.99978	0.99849
		(0.31330)	(0.82490)	(6.3750)

<sup>a</sup>The average absolute percent deviation (AAD%) for the total, thermal, and internal pressures are given in parentheses for each isotherm, within pressure range ( $\Delta p$ ). <sup>b</sup>AAD% =  $(100/n) \sum_{i=1}^n |(p_{\text{emp}} - p_{\text{cal}})/p_{\text{emp}}|$ .

of EoS-III onto the calculated values obtained from the empirical EoS of argon is quite good, except for the critical region ( $150 < T < 200$  K). The critical temperature of argon is 150.687 K.<sup>53</sup> A similar investigation has been carried out for nitrogen ( $\text{N}_2$ ) ( $T_c = 126.192$  K<sup>54</sup>), water ( $\text{H}_2\text{O}$ ) ( $T_c = 647.096$  K<sup>55</sup>), and methane ( $\text{CH}_4$ ) ( $T_c = 190.564$  K<sup>56</sup>), using their empirical EoSs given in refs 57, 58, and 59, respectively. As in Table 2, from the results given in Table 3, we may conclude that EoS-III is accurate for all isotherms, except for those supercritical within the critical region; however, neither eq 3a nor eq 3b fit onto the thermal and internal contributions, respectively, if a wide density range is considered.

Table 3. Same as Table 2 for N<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub> Fluids

T (K)	$\Delta p$ (MPa)	R <sup>2</sup> (AAD%)		
		Z	Z <sub>th</sub>	Z <sub>in</sub>
nitrogen				
120	4–320	0.9999 (1.226)	0.9999 (0.1070)	0.9999 (1.839)
130	0–480	0.9991 (13.78)	0.9949 (6.942)	0.9644 (22.37)
140	0–495	0.9994 (8.782)	0.9971 (5.265)	0.9752 (20.05)
150	0–530	0.9995 (5.965)	0.9979 (4.176)	0.9825 (17.71)
250	0–990	0.9999 (0.7740)	0.9997 (1.399)	0.9988 (12.03)
500	0–1550	1.000 (0.1270)	0.9999 (0.2960)	0.9999 (3.521)
water				
600	13–940	0.9999 (1.256)	0.9988 (0.5970)	0.9919 (0.9670)
630	20–1000	0.9999 (0.5040)	0.9975 (1.437)	0.9878 (1.840)
700	0–560	0.9937 (5.428)	0.9782 (5.615)	0.9496 (11.68)
800	0–750	0.9985 (1.871)	0.9951 (2.729)	0.9857 (7.297)
900	0–930	0.9996 (0.8570)	0.9985 (1.541)	0.9945 (5.067)
1000	0–1100	0.9998 (0.4660)	0.9994 (0.9030)	0.9976 (3.624)
methane				
180	4–450	0.9999 (1.217)	0.9998 (0.2880)	0.9991 (2.302)
185	5–460	0.9999 (2.019)	0.9998 (0.4080)	0.9989 (2.717)
192	0–540	0.9988 (33.95)	0.9936 (7.246)	0.9546 (28.21)
200	0–700	0.9987 (11.61)	0.9944 (6.370)	0.9554 (24.08)
220	0–640	0.9994 (6.430)	0.9968 (4.804)	0.9780 (19.42)
250	0–810	0.9998 (3.318)	0.9984 (3.271)	0.9916 (15.84)
300	0–920	0.9999 (1.546)	0.9993 (2.025)	0.9964 (12.68)

### 3. DENSITY DEPENDENCY OF THERMAL PRESSURE

In this section, the density dependency of the thermal pressure,  $p_{th}$ , and hence the contribution of thermal pressure on the compressibility factor,  $Z_{th} = p_{th}/\rho RT$ , are investigated by different approaches.

**3.1. Using Modified Hard Sphere (HS) EoS.** In many references, the EoSs for the hard sphere model have been substituted for the repulsion term in the famous EoSs to obtain the EoS for the real fluids.<sup>60</sup> In a simple EoS like van der Waals, the thermal pressure is due to the repulsion interactions, then we may use the hard sphere EoS to present the thermal pressure of a real fluid. However to make the presentation accurate, we shall make two modifications on the HS-EoS as follows: (1) Unlike hard spheres, real molecules penetrate each other to some extent; therefore, molecular diameter is temperature dependent. (2) In addition to the mean molecular separations, the interactions among molecules change with

temperature as well; hence, unlike the HS model, the coefficients of eq 3a for a real fluid are expected to be temperature dependent.

#### 3.1.1. Temperature Dependency of Molecular Diameter.

An accurate virial equation with sixteen terms has been reported for the HS fluid,<sup>61,62</sup> by using molecular dynamics simulations as

$$Z = 1 + 4y + 10y^2 + 18.3648y^3 + 28.2245y^4 + \dots \quad (4)$$

where  $y = \pi\rho\sigma^3/6$  is the packing fraction for the spheres with the diameter  $\sigma$ . At very low densities,  $Z$  can be written in terms of  $y$  as

$$Z = 1 + 4y \quad (5)$$

If we use the empirical EoS of a fluid to calculate its thermal pressure, and hence  $Z_{th} = p_{th}/\rho RT$ , and substitute  $Z_{th}$  for  $Z$  in eq 5, for an isotherm at low densities, we can obtain its molecular diameter at that temperature. Such investigation has been carried out for CH<sub>4</sub>, Ar, N<sub>2</sub>, and oxygen (O<sub>2</sub>) fluids (their empirical EoSs are given in refs 52, 57, 59, and 63, respectively), for which the molecular attractions are weak and not very far from the HS. The results are shown in Figure 3. As shown in this figure, the diameter decreases with

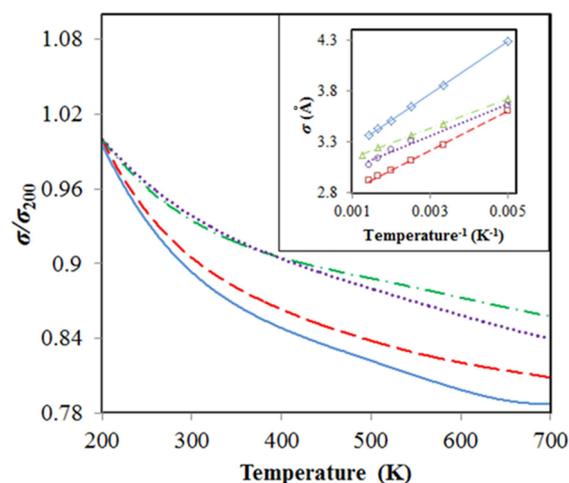


Figure 3. Molecular diameter versus  $T$  and  $1/T$  (inset) for methane<sup>58</sup> (solid blue), argon<sup>52</sup> (dashed red), oxygen<sup>65</sup> (dotted purple), and nitrogen<sup>56</sup> (dashed–dotted green).  $\sigma_{200}$  is the molecular diameter at  $T = 200$  K.

temperature, which is in accordance with those reported in literature.<sup>64–66</sup> On the basis of Figure 3 (inset), the molecular diameter varies almost linearly with  $1/T$  as

$$\sigma = \sigma_0 + \frac{\sigma_1}{T} \quad (6)$$

where  $\sigma_0$  is the molecular diameter at very high temperatures which may be considered as the hard core diameter of the molecule.

**3.1.2. Temperature Dependence of Thermal Compressibility Factor.** The Carnahan–Starling EoS<sup>67</sup> (CS-EoS) is an accurate closed-form EoS that has been proposed for the hard sphere fluid

$$Z_{CS} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} \quad (7)$$

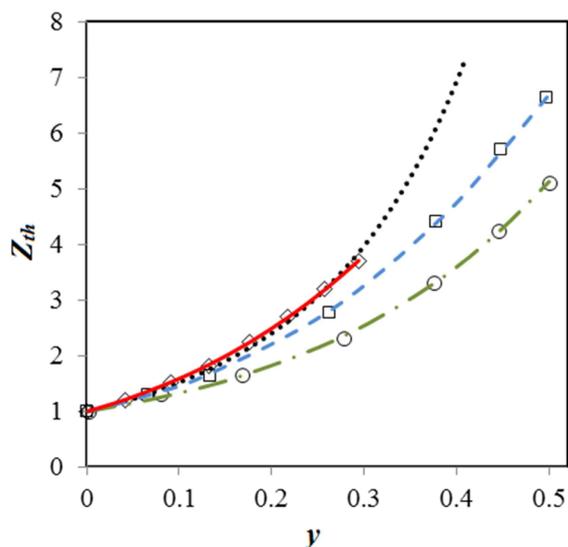
We shall use the CS-EoS to describe the thermal pressure of a real fluid, but in addition to temperature dependency of the molecular diameter discussed before, the coefficients 1 and  $-1$  of the  $y^2$  and  $y^3$  terms, respectively, in the numerator of eq 7 will be assumed to be temperature dependent and will be denoted by  $\alpha(T)$  and  $\beta(T)$ . Due to argument given in the section 3.1.1, we have to consider the coefficients of the  $y$  terms in eq 7 temperature independent. A similar correction was applied by Boublik for the nonsphericity of real molecules.<sup>68</sup> Including these two modifications in the CS-EoS, resulted in the following expression for the thermal compressibility factor of a real fluid

$$Z_{CS}^{mod} = \frac{1 + y + \alpha(T)y^2 + \beta(T)y^3}{(1 - y)^3} \quad (8a)$$

which will be referred to the modified Carnahan–Starling equation of state (MCS-EoS) hereafter. The MCS-EoS may be written in the virial form as

$$Z = 1 + 4y + (9 + \alpha)y^2 + (16 + 3\alpha + \beta)y^3 + (25 + 6\alpha + 3\beta)y^4 + (36 + 10\alpha + 6\beta)y^5 + \dots \quad (8b)$$

Unlike eq 2, this equation and hence  $Z_{th}$ , is expected to include all powers of density. We have also used the empirical EoS of Ar<sup>52</sup> to calculate its thermal pressure and hence  $Z_{th}$ . Then eq 8a is fitted onto the calculated results for the 200, 300, 400, 500, 600, and 700 K isotherms and compared to the CS-EoS. As shown in Figure 4, the MCS-EoS fits well onto the  $Z_{th}$



**Figure 4.** Fits of  $Z_{th}$  for Ar, obtained from its empirical EoS, by the MCS-EoS for the 200 (○), 300 (□), and 700 K (◇) isotherms. The dotted line shows the CS-EoS for the hard sphere fluid.

for the three shown isotherms (200, 300, and 700 K), with  $R^2 > 0.996$  and  $AAD\% < 1.3$  (for  $p_{th}$ ). The results for the calculated pressure of six isotherms are summarized in Table 4. Also at high temperatures, argon behaves like a hard sphere fluid; therefore, its  $Z_{th}$  approaches to that of HS. See the 700 K isotherm in Figure 4 and the results for 500, 600, and 700 K in Table 4.

**3.2. Using the Accurate Semiempirical Redlich–Kwong EoS.** On the basis of vdW-EoS

**Table 4.** Coefficient of Determination and the Average Absolute Percent Deviation of Pressure and Its Maximum Value for Fitting MCS-EoS onto the Calculated  $Z_{th}$  Obtained from the Empirical EoS for the Given Isotherms of Argon<sup>a</sup>

T(K)	$R^2$	AAD% (Max)	
		$p_{th} - p_{fit}$	$p_{th} - p_{HS}$
200	0.9965	1.119 (4.125)	31.54 (60.66)
300	0.9996	0.8964 (2.647)	20.00 (48.27)
400	0.9999	0.4908 (1.246)	8.501 (25.93)
500	1.000	0.0941 (0.2402)	3.822 (14.33)
600	1.000	1.236 (2.091)	2.667 (7.877)
700	1.000	0.6450 (1.607)	2.491 (4.496)

<sup>a</sup>The quantities  $p_{fit}$  and  $p_{HS}$  are the fitting and HS pressures obtained from eqs 8a and 7, respectively.

$$p = \frac{RT}{v_m - b} - \frac{a}{v_m^2} \quad (9)$$

the thermal pressure may be obtained as

$$p_{th} = T \left( \frac{\partial p}{\partial T} \right)_\rho = \frac{RT\rho}{1 - b\rho} \quad (10a)$$

If eq 9 is expanded as a power series of density we will have

$$Z_{th} = 1 + (b\rho + b^2\rho^2 + b^3\rho^3 + b^4\rho^4 + \dots) \quad (10b)$$

We, also see that according to vdW EoS, the cubic term of density is present in  $Z_{th}$ . However, the vdW EoS predicts that only repulsion interactions contribute in  $Z_{th}$ . But as explained in the previous section, the attractions among particles are expected to contribute in  $Z_{th}$ , as well. Such expectation is in accordance with the RK-EoS,<sup>26</sup>

$$p = \frac{RT}{v_m - b} - \frac{a}{v_m(v_m + b)T^{1/2}} \quad (11)$$

from which we may obtain the thermal pressure as

$$\begin{aligned} p_{th} &= T \left( \frac{R\rho}{1 - b\rho} + \frac{a\rho^2}{2T^{3/2}(1 + b\rho)} \right) \\ &= RT\rho + \left( \frac{a}{2b\sqrt{T}} + RT \right) b\rho^2 + \left( -\frac{a}{2b\sqrt{T}} + RT \right) b^2\rho^3 \\ &\quad + \left( \frac{a}{2b\sqrt{T}} + RT \right) b^3\rho^4 + \left( -\frac{a}{2b\sqrt{T}} + RT \right) b^4\rho^5 \\ &\quad + \dots \end{aligned} \quad (12)$$

Therefore, we may conclude from both vdW and RK EoS that the thermal compressibility factor cannot simply be presented by eq 3a.

**3.3. Calculation of the Thermal Pressure via an Accurate Empirical EoS.** In section 1 we saw that the thermal compressibility factor could not be described by a simple three-term expression of eq 3a. However,  $Z_{th}$  obtained from the empirical EoS of argon<sup>52</sup> may be well fitted by

$$Z_{th} = 1 + e_{th}\rho^2 + f_{th}\rho + g_{th}\rho^4 + h\rho^3 \quad (13)$$

in which the  $\rho^3$  term is added to eq 3a. Figure 1b shows how well  $Z_{th}$  for the 180 K isotherm of argon is fitted by eq 13 compared to that of eq 3a. The results of similar fittings are summarized in Table 5 for some other isotherms, as well, in

**Table 5. Coefficient of Determination ( $R^2$ ) for Fitting  $Z_{th}$  and  $Z_{in}$  Calculated from the Empirical EoS, by Equations 13 and 16, Respectively, along with the Values of Their Coefficients, for the Given Isotherms of  $Ar^4$** 

	$T$ (K)	$R^2$	$e \times 10$ (L/mol) <sup>2</sup>	$f \times 10^2$ (L/mol)	$h \times 10^3$ (L/mol) <sup>3</sup>	$g \times 10^5$ (L/mol) <sup>4</sup>	AAD%
$Z_{in}$	145	1.00000	2.91	-2.99	0.540	$-4.34 \times 10^{-10}$	0.0001
	150	1.00000	3.95	-3.56	0.621	$-4.67 \times 10^{-10}$	0.0001
	151	0.99342	-2.38	2.04	-0.998	1.53	8.953
	160	0.99823	-1.97	1.54	-0.796	1.29	5.439
	165	0.99897	-1.83	1.38	-0.726	1.19	5.648
	180	0.99965	-1.54	1.06	-0.582	1.00	3.967
	200	0.99985	-1.28	0.792	-0.451	0.820	3.282
	300	0.99999	-0.679	0.286	-0.185	0.411	0.8270
	400	0.99999	-0.453	0.157	-0.105	0.270	2.738
$Z_{th}$	145	0.99987	-2.70	2.50	-0.540	0.457	0.392
	150	0.99971	-3.95	3.19	-0.621	0.417	1.191
	151	0.99762	1.99	-2.21	0.998	-1.18	3.104
	160	0.99886	1.64	-1.70	0.796	-0.945	2.532
	165	0.99893	1.51	-1.53	0.726	-0.862	2.887
	180	0.99933	1.31	-1.20	0.582	-0.686	2.291
	200	0.99953	1.08	-0.890	0.451	-0.529	1.821
	300	0.9999	0.642	0.275	0.185	-0.217	0.724
	400	0.99998	0.483	-0.094	0.105	-0.128	0.298

<sup>a</sup>The average absolute percent deviation of pressure is given, as well.

**Table 6. Same as Table 5 for  $N_2$ ,  $H_2O$ , and  $CH_4$  Fluids**

	$T$ (K)	$R^2$	$e \times 10$ (L/mol) <sup>2</sup>	$f \times 10^2$ (L/mol)	$h \times 10^3$ (L/mol) <sup>3</sup>	$g \times 10^5$ (L/mol) <sup>4</sup>	AAD%	
$N_2$	$Z_{in}$	130	0.99804	-2.57	2.44	-14.9	30.0	0.342
		140	0.99917	-2.14	1.83	-11.7	23.3	6.01
		150	0.99948	-1.83	1.41	-9.40	20.0	3.99
		250	0.99983	-0.705	0.174	-2.00	6.64	2.99
		500	0.99995	-0.240	-0.038	-0.051	2.14	2.10
	$Z_{th}$	130	0.99853	2.25	-2.76	14.9	-20.0	0.119
		140	0.99915	1.85	-2.09	11.7	-15.9	3.07
		150	0.99940	1.56	-1.61	9.40	-10.0	2.59
		250	0.99998	0.643	-0.132	2.00	-2.51	2.09
		500	0.99999	0.391	0.185	0.051	-0.058	0.259
$H_2O$	$Z_{in}$	600	0.99999	2.12	-1.68	3.00	-1.46	0.032
		630	0.99636	2.90	-1.88	3.11	-1.52	0.778
		700	0.99764	-2.22	1.27	-3.58	3.40	2.41
		800	0.99965	-1.45	0.636	-1.72	1.72	1.18
		900	0.99982	-1.05	0.350	-0.929	1.01	0.774
	$Z_{th}$	1000	0.99985	-0.796	0.198	-0.513	0.635	0.601
		600	0.99995	-2.53	1.68	-3.00	1.83	0.115
		630	0.99928	-3.09	1.82	-3.11	1.83	0.739
		700	0.99760	1.69	-1.19	3.58	-3.22	1.61
		800	0.99954	1.07	-0.571	1.72	-1.537	0.630
$CH_4$	$Z_{in}$	900	0.99981	0.772	-0.294	0.929	-0.830	0.363
		1000	0.99988	0.594	-0.148	0.513	-0.466	0.271
		180	0.99924	2.84	-3.69	4.70	12.4	2.11
		185	0.99900	1.29	-1.94	-1.47	19.5	2.69
		192	0.99479	-2.93	3.18	-21.1	43.8	11.6
	$Z_{th}$	200	0.99672	-2.78	3.00	-20.2	42.5	6.64
		220	0.99686	-2.06	1.80	-13.2	30.4	6.21
		250	0.99730	-1.42	0.806	-7.24	19.8	6.25
		300	0.99867	-1.03	0.35	-4.12	13.6	6.84
		180	0.99984	-2.53	2.79	-4.70	1.87	0.391
$Z_{th}$	185	0.99987	-1.07	1.13	1.47	-5.82	0.356	
	192	0.99809	2.49	-3.53	21.1	-32.5	2.88	
	200	0.99840	2.35	-3.31	20.2	-31.7	2.64	
	220	0.99905	1.69	-2.03	13.2	-20.6	1.78	
	250	0.99943	1.10	-0.929	7.24	-11.2	0.992	
	300	0.99976	0.805	-0.372	4.12	-6.57	0.535	

which the coefficient of determination, average absolute percent deviation of pressure, and coefficients of eq 13 are given. As shown in this table, the fitting is done well for all isotherms with  $R^2 > 0.997$  and  $AAD\% < 3.1$  for pressure (these numbers may be compared with 0.995 and 5.64, respectively, given in Table 3 when the  $\rho^3$  term is not included). However, the deviation for the supercritical isotherms within the critical region is the largest. Similar investigation carried out for  $N_2$ ,  $H_2O$ , and  $CH_4$  using their empirical EoSs, for which the results are summarized in Table 6.

#### 4. DENSITY DEPENDENCY OF INTERNAL PRESSURE

In this section, the possibility of expressing the internal compressibility factor by eq 3b will be investigated by using the vdW, RK, and empirical EoSs.

##### 4.1. Calculation of $Z_{in}$ Using Two Semiempirical EoSs.

On the basis of vdW-EoS,  $Z_{in}$  may be given as

$$Z_{in} = -\frac{a}{RT}\rho \quad (14)$$

According to which  $Z_{in}$  is linear in density for each isotherm. This prediction is quite different with that shown in Figure 2. We may use a significantly more accurate semiempirical EoS, namely RK, to obtain  $p_{in}$  and  $Z_{in}$ . According to RK-EoS

$$p_{in} = -\left(\frac{\partial E}{\partial v}\right)_T = \rho^2 \left(\frac{\partial E}{\partial \rho}\right)_T = -\frac{3a\rho^2}{2\sqrt{T}} + \frac{3ab\rho^3}{2\sqrt{T}} - \frac{3ab^2\rho^4}{2\sqrt{T}} + \frac{3ab^3\rho^5}{2\sqrt{T}} + \dots \rightarrow Z_{in} = \left(\frac{3}{2}aR\sqrt{T}\right) (-\rho + b\rho^2 - b^2\rho^3 + b^3\rho^4 + \dots) \quad (15)$$

We notice that the RK-EoS predicts all powers of density for  $Z_{in}$ , similar to eq 13 for  $Z_{th}$ , except for term 1.

**4.2. Calculation of Internal Pressure via an Accurate Empirical EoS.** In section 2, we saw the failure of eq 3b to describe  $Z_{in}$  in a wide density range. On the basis of the previous subsection, if the cubic term of density is added to eq 3b, we will have

$$Z_{in} = \frac{p_{in}}{\rho RT} = e_{in}\rho^2 + f_{in}\rho + g_{in}\rho^4 + h_{in}\rho^3 \quad (16)$$

To investigate the validity of eq 16, the calculated internal compressibility factor obtained from an empirical EoS may be fitted by this equation. Figure 2 shows how well eq 16 is fitted onto the internal compressibility factor of the 180 K isotherm of argon ( $R^2 = 0.9996$ ), compared to the fitting of eq 3a with  $R^2 = 0.9797$ . Table 5 shows the parameters of eqs 13 and 16 along with the coefficients of determination of fitting and  $AAD\%$  of pressure for the given isotherms of argon. Note that the  $AAD\%$  is less than 8.9 and  $R^2 > 0.993$  for eq 16, while those values are 22.6 and 0.945, respectively, for eq 3a (see Table 5). Since eq 2 well fits onto the compressibility factor (see Figure 1), to obtain the coefficient of eq 16 we have used the following constraint

$$h_{in} = -h_{th} \quad (17)$$

As shown in Table 5, eqs 13 and 16 well fit onto the  $Z_{th}$  and  $Z_{in}$ , respectively, for all isotherms, except those supercriticals close to the critical temperature (i.e., 151, 160, and 165 K). The coefficients of determination for similar fittings for some isotherms of  $N_2$ ,  $H_2O$ , and  $CH_4$  are summarized in Table 6. As in Table 5, from the results given in Table 6, we may conclude that unlike eqs 3a and 3b, eqs 13 and 16 represent  $Z_{th}$  and  $Z_{in}$

well, respectively, except for isotherms nearby the critical isotherm.

#### 5. CRITICAL REGION

Even though EoS-III is accurate for all types of solids and fluids, it shows a significant deviation for supercritical isotherms near the critical temperature. The coefficient of determination of fitting  $p\rho T$  data onto EoS-III for different isotherms are shown in Figure 5 for Ar,  $NH_3$ ,  $CH_4$ ,  $N_2$ ,  $CH_3OH$ , and  $C_4H_{10}$  fluids.

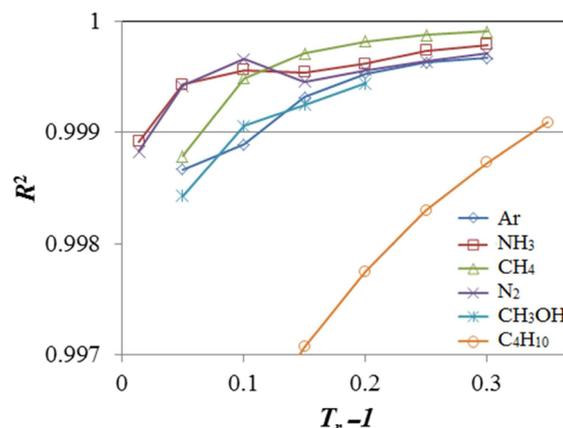


Figure 5. Coefficient of determination for fitting eq 2 onto  $p\rho T$  data of some given fluids (the lines are drawn to guide the eye).

One may notice that the fitting for spherical or almost spherical species (Ar,  $NH_3$ ,  $CH_4$ ,  $N_2$ , and  $CH_3OH$ ) is well done with  $R^2 > 0.999$ , except for isotherms within  $1 \leq T_r = T/T_c \leq 1.1$ . However the upper reduced temperature may be larger for the cylindrical molecules, like  $C_4H_{10}$ .

The aim in this section is to modify EoS-III in such a way that it well presents the  $p\rho T$  data of real fluids within the critical region, as well. We may start from the RK-EoS, whose density expansion is

$$Z = 1 + \left(b - \frac{a}{RT^{3/2}}\right)\rho + \left(b + \frac{a}{RT^{3/2}}\right)b\rho^2 + \left(b - \frac{a}{RT^{3/2}}\right)b^2\rho^3 + \left(b + \frac{a}{RT^{3/2}}\right)b^3\rho^4 + \dots \quad (18)$$

where  $b$  and  $a/RT^{3/2}$  are related to the repulsion and attraction interactions among molecules, respectively. For a simple fluid like Ar, with no long-range attractions, due to the balance of attraction and repulsion forces, the coefficient  $b - a/RT^{3/2}$  (and its corresponding coefficient in the vdW-EoS, i.e.,  $b - a/RT$ ) is expected to vanish.<sup>19</sup> Therefore, all odd powers of  $\rho$  in eq18 become zero, then it leads to the LIR-EoS,<sup>19</sup> if the higher order terms are discarded

$$Z = 1 + A\rho^2 + B\rho^4 \quad (19)$$

where  $A$  and  $B$  are temperature dependent parameters. The fact that on the basis of EoS-III the  $\rho$  term exists, while the  $\rho^3$  term is absent, we may expect that the coefficient  $b(1 - a/bRT^{3/2})$  is not zero but is small, in such a way that if it is multiplied by  $b^2\rho^3$  it becomes insignificant ( $b\rho < 1$ ). Note that for the same reason, all coefficients of the  $\rho^n$  terms with  $n > 4$  are insignificant and therefore not appear in EoS-III.

However, for the critical region (isotherms within  $1 \leq T/T_c \leq 1.1$ , for the spherical or near spherical molecules), due to very long correlation length, we may expect that the attraction contribution,  $a/RT^{3/2}$ , is significantly larger than the repulsion contribution,  $b$ , in such a way that the  $\rho^3$  term has to be included, which leads to

$$Z = 1 + \alpha_1\rho + \alpha_2\rho^2 + \alpha_3\rho^3 + \alpha_4\rho^4 \quad (20)$$

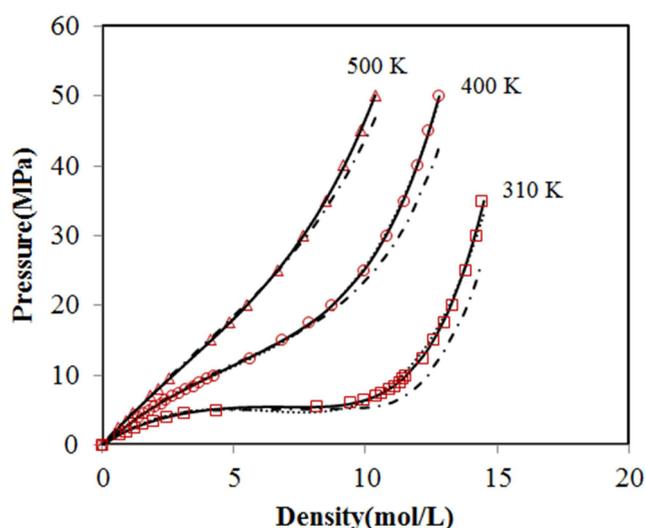
which will be referred to the modified EoS-III (EoS-MIII). Owing to the fact that the long-range correlation is given a more significant weight, compared to EoS-III, we may expect that EoS-MIII becomes more accurate for the critical region. To examine such expectation, we shall see how well this EoS fits onto the values obtained from the empirical EoS. Table 7

**Table 7. Coefficient of Determination and the Average Absolute Percent Deviation of Pressure for EoS-III and EoS-MIII for Given Isotherm(s) Nearby the Critical Temperature**

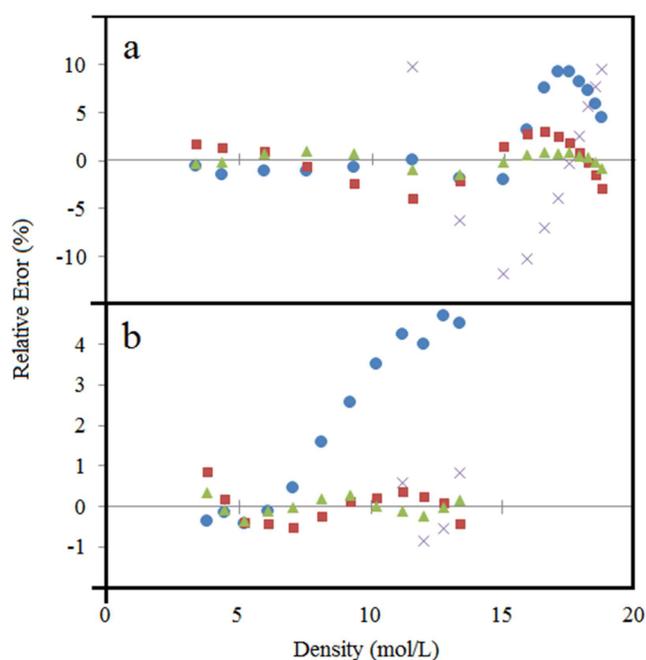
	T (K)	EoS-III		EoS-MIII	
		R <sup>2</sup>	AAD%	R <sup>2</sup>	AAD%
H <sub>2</sub> O (647.14) <sup>a</sup>	650	0.99571	10.391	0.99962	2.4567
	700	0.99735	4.4980	0.99988	0.99843
O <sub>2</sub> (154.59)	160	0.99304	3.0528	0.99974	0.32437
	180	0.99633	1.7365	0.99983	0.27746
CO <sub>2</sub> (304.13)	310	0.99729	6.9240	0.99997	0.58288
	330	0.99856	5.3916	0.99998	0.56799
CH <sub>3</sub> OH (512.50)	515	0.99670	11.105	0.99987	2.9143
	530	0.99783	6.8425	0.99989	1.9612
CH <sub>4</sub> (190.56)	195	0.99885	14.126	0.99995	1.4186
	375	0.99288	8.2261	0.99969	1.0297
C <sub>3</sub> H <sub>8</sub> (369.83)	390	0.99394	4.5040	0.99972	0.53624
	550	0.99258	3.7364	0.99965	0.51680
C <sub>7</sub> H <sub>16</sub> (540.20)	567	0.99301	4.3414	0.99950	0.57025
	580	0.99086	3.7804	0.99953	0.43743
Ar (150.87)	151	0.99713	12.824	0.99995	1.5043
	160	0.99825	8.8404	0.99998	0.82493
Xe (289.77)	295	0.99605	11.563	0.99985	2.1842
	310	0.99731	16.283	0.99988	2.1431
NH <sub>3</sub> (405.50)	410	0.99832	5.7354	0.99990	1.2321
	R114 (418.78)	425	0.98792	10.629	0.99796
R134a (374.18)	380	0.98786	4.1149	0.99946	1.3831
	R218 (345.10)	350	0.98463	5.0491	0.99771
SF <sub>6</sub> (318.69)	380	0.99132	4.4172	0.99898	1.3793
	323	0.98770	4.7460	0.99910	0.80851
	330	0.98947	4.2032	0.99941	0.74003

<sup>a</sup>Critical temperatures taken from ref 72 are given in parentheses.

shows the superiority of EoS-MIII over EoS-III in fitting onto the data obtained from the empirical EoS<sup>69</sup> of fifteen different fluids within the critical region. We have fitted EoS-III, EoS-MIII, and EoSSCF + RG<sup>39</sup> to  $pVT$  data of ethane<sup>70</sup> for three isotherms (310, 400, and 500 K) to obtain their coefficients. Having the coefficients, we may calculate the pressure given by each EoS and compare to that of EoS-III + RG.<sup>38</sup> The results are compared to experimental values in Figure 6. Similar comparison has been carried out for the 315 and 350 K isotherms of CO<sub>2</sub>.<sup>69</sup> The deviation curves for EoS-MIII, EoS-III, LIR-EoS, and CPR-EoS<sup>37</sup> are shown in Figure 7, and AAD % of pressure for each EoS is given in Table 8. The superiority of EoS-MIII over the other EoSs may be noticed from Figure 7



**Figure 6.** Calculated pressure against density for the supercritical isotherms of ethane obtained from EoS-MIII (solid curve), EoS-III (dotted curve) and EoS-III + RG (dotted-dashed curve). Experimental values for 310 (□), 400 (○), and 500 K (△) isotherms are shown.



**Figure 7.** Percent pressure deviation of EoS-III (■), EoS-MIII (▲), LIR (×), and CPR-EoS (●) for (a) 315 and (b) 350 K isotherms of CO<sub>2</sub>.

**Table 8. Average Absolute Percent Deviation of Pressure for 315 and 350 K Isotherms of CO<sub>2</sub> Calculated from EoS-MIII, EoS-III, LIR-EoS, and CPR-EoS, along with the Maximum Deviation for Each Isotherm**

	AAD% (max)	
	T = 315 K	T = 350 K
EoS-MIII	0.6340(1.576)	0.1632(0.3575)
EoS-III	1.871(4.009)	0.3354(0.8581)
LIR-EoS	6.794(11.96)	0.7007(0.8546)
CPR-EoS	3.967(9.144)	2.227(4.710)

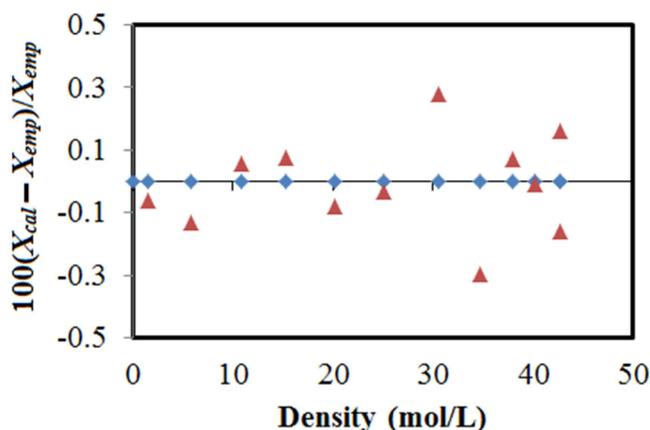
and Table 8. Note that the quantity AAD% for EoS-MIII is smaller than that for other EoSs at least by a factor of 3.

## 6. THERMODYNAMIC PROPERTIES OUTSIDE THE CRITICAL REGION

Using eq 16, we may calculate the internal pressure, from which the internal energy can be derived for each isotherm as

$$E = \int \frac{p_{in}}{\rho^2} d\rho + F(T) \\ = RT \left( \frac{e_{in}}{2} \rho^2 + f_{in} \rho + \frac{g_{in}}{4} \rho^4 + \frac{h_{in}}{3} \rho^3 \right) + F(T) \quad (21)$$

where  $F(T)$  is the ideal contribution to the total internal energy and for a monatomic ideal gas like argon is equal to  $3RT/2$  per mole. It means that the internal energy is a quadric function in terms of density for each isotherm. To investigate the accuracy of eq 21, the internal energy for the 400 K isotherm of argon has been calculated using the coefficients of eq 16 for this isotherm ( $e_{in} = 1.568 \times 10^{-3}$  (L/mol)<sup>2</sup>,  $f_{in} = -4.527 \times 10^{-2}$  L/mol,  $g_{in} = 2.704 \times 10^{-6}$  (L/mol)<sup>4</sup>, and  $h_{in} = -1.053 \times 10^{-4}$  (L/mol)<sup>3</sup>). Percent deviation of the calculated internal energy using eq 21, compared to the empirical value,<sup>69</sup> is shown in Figure 8. We see that the predicted values are very accurate.



**Figure 8.** Percent deviation of the calculated internal energy (◆) and enthalpy (▲), compared to the empirical values<sup>69</sup> for the 400 K isotherm of argon.

By having  $E$  from eq 21 and  $pv$  from eq 2, the enthalpy may be given by

$$H = RT \left[ \left( \frac{e_{in}}{2} + e \right) \rho^2 + (f_{in} + f) \rho + \left( \frac{g_{in}}{4} + g \right) \rho^4 + \frac{h_{in}}{3} \rho^3 \right] + F(T) \quad (22)$$

Figure 8 also shows the accuracy of eq 22 ( $e = 6.310 \times 10^{-4}$  (L/mol)<sup>2</sup>,  $f = 2.989 \times 10^{-3}$  (L/mol), and  $g = 1.427 \times 10^{-6}$  (L/mol)<sup>4</sup>) in predicting the enthalpy of 400 K isotherm of Ar, with the percent deviation less than 0.3.

Also, we may obtain the heat capacities at constant volume and constant pressure,  $C_v$  and  $C_p$ , simply by taking partial derivatives of  $E$  and  $H$  with respect to  $T$ , respectively

$$C_v = R \left[ \left( \frac{e_{in} + e'_{in}T}{2} \right) \rho^2 + (f_{in} + f'_{in}T) \rho + \left( \frac{g_{in} + g'_{in}T}{4} \right) \rho^4 + \left( \frac{h_{in} + h'_{in}T}{3} \right) \rho^3 \right] + F'(T) \quad (23)$$

$$C_p = R \left[ \left( \frac{e_{in} + e'_{in}T}{2} + e + e'T \right) \rho^2 + \{f_{in} + f + (f'_{in} + f')T\} \rho + \left( \frac{g_{in} + g'_{in}T}{4} + g + g'T \right) \rho^4 + \left( \frac{h_{in} + h'_{in}T}{3} \right) \rho^3 \right] + F'(T) \quad (24)$$

where the prime signs show the temperature derivatives.

Finally, we may obtain entropy as a function of density for an isotherm as

$$S = \int \frac{C_p}{T} dT + \text{const} \\ = S_0(T) + S_1(T)\rho + S_2(T)\rho^2 + S_3(T)\rho^3 + S_4(T)\rho^4 \quad (25)$$

where  $S_0(T)$  is the ideal contribution to the total entropy and

$$\frac{S_1(T)}{R} = \int [(f_{in} + f + (f'_{in} + f')T)/T] dT \quad (26)$$

$$\frac{S_2(T)}{R} = \int \left[ \left( \frac{e_{in} + e'_{in}T}{2} + e + e'T \right) / T \right] dT \quad (27)$$

$$\frac{S_3(T)}{R} = \int \left[ \left( \frac{h_{in} + h'_{in}T}{3} \right) / T \right] dT \quad (28)$$

$$\frac{S_4(T)}{R} = \int \left[ \left( \frac{g_{in} + g'_{in}T}{4} + g + g'T \right) / T \right] dT \quad (29)$$

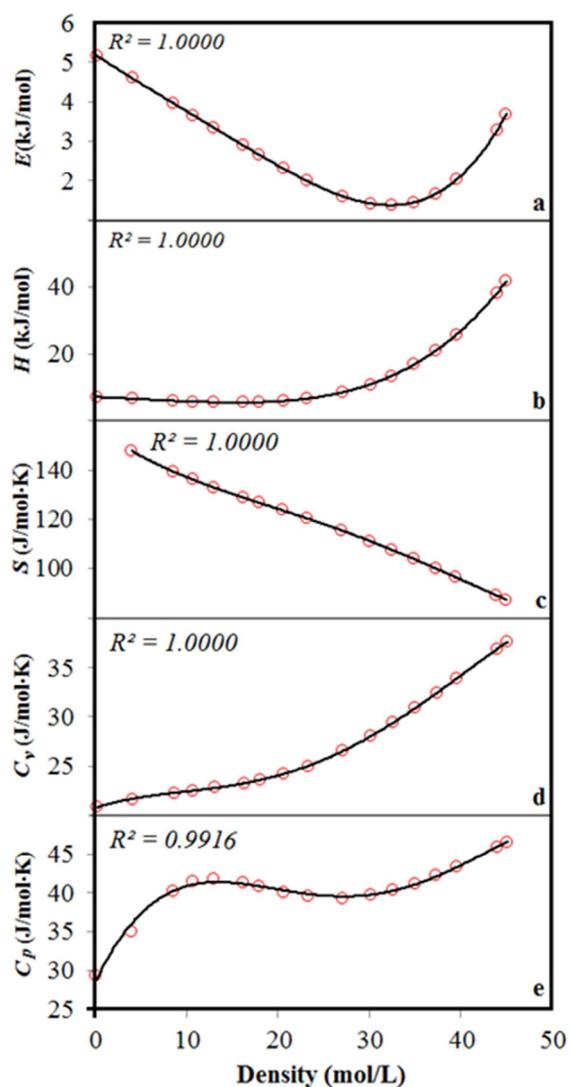
We see that each thermodynamic property mentioned above can be expressed as a quadric function in density for each isotherm. Figure 9 shows such dependencies for the 250 K isotherm of nitrogen,<sup>69</sup> along with the coefficients of determination for the fittings.

## 7. SUMMARY AND CONCLUSION

A simple three-term EoS, namely EoS-III, has been found to be accurate for describing  $pvT$  behavior of all types of fluids in wide temperature and pressure ranges, except for the isotherms within the critical region. In this paper, the validity of similar three-term expressions for both thermal and internal pressures have been investigated.

Using the empirical EoS for some fluids, the thermal pressure has been calculated and fitted onto eq 3a. Also, the internal pressure has been obtained by subtracting the thermal pressure from the total pressure and fitted it onto eq 3b. We have noticed that, unlike the total pressure, neither its thermal nor its internal components fit onto eqs 3a and 3b, respectively, if a wide density range is considered (see Tables 2 and 3).

Then, the density dependencies of thermal and internal pressures have been investigated by several approaches. The



**Figure 9.** Density dependencies of (a) internal energy, (b) enthalpy, (c) entropy, and heat capacity at (d) constant volume and (e) constant pressure, each as a quadric function, for the 250 K isotherm of  $N_2$  (experimental data (O) are taken from ref 69).

thermal pressure of a real fluid has been calculated from the HS-EoS, namely the Carnahan–Starling EoS, but with two modifications: (1) the coefficients of EoS are considered to be temperature dependent and (2) molecular diameter also is assumed to be temperature dependent (Figure 3). The latter dependency is due to the fact that the real molecules can penetrate each other, especially at high temperatures. We have then used the MCS-EoS to present the thermal pressure which is found to be accurate in a wide density range, at least for Ar (see Figure 4). If the MCS-EoS is expanded in terms of density, all powers of density are present then the thermal pressure, unlike eq 3a, includes the other terms of density, as well. Also, using a quite accurate<sup>51</sup> two-parameter RK-EoS, it is found that all powers of density should be contributed in the thermal compressibility factor and hence in the thermal pressure. On the basis of these two approaches we have concluded that it is at least necessary to add a cubic term in density to the expression for  $Z_{th}$ , however, the other terms in density may be also important especially in the critical region (see Tables 5 and 6). Therefore, eq 3a has been modified for isotherms far from

the critical temperature by adding the  $\rho^3$  term. Finally the calculated  $Z_{th}$  obtained from the accurate empirical EoS has been fitted onto modified eq 3a (eq 13) for four different fluids and it noticed that eq 13 is accurate for isotherms not in the critical region (Figure 1 and Tables 5 and 6). Also, in order to find an appropriate expression for the internal compressibility factor, we used RK-EoS again and obtained the internal pressure from  $p_{in} = p - p_{th}$ . In this case again we have shown that all powers of density are present which is in accordance with the calculated  $Z_{in}$  obtained from the empirical EoS (see Figure 2 and Tables 5 and 6). Note that for isotherms, not in the critical region, although the vdW-EoS can fairly fit onto experimental  $pVT$  data; the linear density dependency of the internal compressibility factor predicted by this equation is quite different from experimental values (see Figure 2). So, eq 3b was modified to eq 16 to which simply the  $\rho^3$  term is added. However eq 16 is more accurate for the isotherms far from critical point, compared to those within the critical region (see Tables 5 and 6). Owing to the fact that eqs 13, 16, and 2 are accurate for the thermal, internal, and total compressibility factor, respectively, for an isotherm not nearby the critical temperature, we may conclude that  $h_{in} = -h_{th}$ .

Let consider the Virial EoS,

$$p = RT[\rho + \sum_{i=2} B_i(T)\rho^i] \quad (30)$$

from which the thermal and internal pressures may be obtained as

$$p_{th} = RT[\rho + \sum_{i=2} B_i(T)\rho^i] + RT^2 \sum_{i=2} B'_i(T)\rho^i \quad (31)$$

$$p_{in} = RT^2 \sum_{i=2} B'_i(T)\rho^i \quad (32)$$

where the prime signs show the temperature derivatives. Note that if due to balance of attractive and repulsive forces  $B_2$  is insignificant ( $B_2 \approx 0$ ), then on the basis of the Virial EoS, the term  $\rho^2$  appears on both thermal and internal pressures, but not in the total pressure. A similar situation occurs for the other terms. On the basis of EoS-III, we may conclude that the clusters with four particles have insignificant contribution in the total pressure (note that the  $\rho^4$  term in EoS-III does not exist). Also, the same contribution for the clusters with more than five particles are insignificant. Therefore, it is reasonable to take only the clusters with one, two, and three particles, to calculate the total pressure, such clusters are those which are usually taken into account in the molecular dynamics simulations.

We have noticed that EoS-III is not able to describe the volumetric behavior of the fluids within the critical region (more specifically for isotherms within  $1 \leq T_r \leq 1.1$  of spherical and near spherical species and perhaps for a larger temperature range for the cylindrical molecules; see Figure 5). We have modified EoS-III in such a way that it accurately presents the isotherms within the critical region, by using the fact that all powers of density are present in an accurate semiempirical RK-EoS. It has been noticed that for a simple fluid like argon, with no long-range attractions, all odd powers of density in RK-EoS may be vanished, because the attraction and repulsion interactions cancel out each other, using a similar argument given for LIR-EoS<sup>19</sup> by using vdW-EoS. Due to the long-range correlations in the critical region, such cancellation is not expected to happen, therefore the magnitude of the  $\rho$  term in eq 18 and hence that of the  $\rho^3$  term in this equation are

significant. However, the  $\rho^n$  terms with  $n > 4$  may be discarded, because the quantity  $1 - a/bRT^{3/2}$  must be multiply by the small  $(b\rho)^n$  term to give the coefficient ( $b\rho < 1$ ). The accuracy of such equation, EoS-MIII, for some fluids are shown in Figures 6 and 7, as well as Table 7, even though the cubic equations, which are also known as van der Waals equation's family, which are equivalent to a (mean field) Landau theory, fail to predict the  $p\rho T$  behavior next to the critical point.<sup>72</sup>

Finally, the obtained expression for the internal compressibility factor along with EoS-III is used to derive internal energy, enthalpy, entropy, heat capacity at constant volume, and constant pressure each as a quadric function in density (Figure 9). In order to obtain the temperature dependency of these properties, one should know the temperature dependency of coefficients of eq 16 and their temperature derivatives; see eqs 21–29. This task will remain for the future. Also, the expressions for such properties are more complicated in the critical region, which will be investigated in the future.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail address: Parsafar@sharif.edu. Fax: (+9821) 66005718, 66012983. Phone: (+9821) 66165355.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors would like to thank Prof. E. K. Goharshadi for helpful comments.

## REFERENCES

- (1) Flory, P. J. Statistical thermodynamics of liquid mixtures. *J. Am. Chem. Soc.* **1965**, *87*, 1833–1838.
- (2) Goharshadi, E. K.; Nazari, F. Computation of internal pressure of liquids using a statistical mechanical equation of state. *Fluid Phase Equilib.* **2001**, *187–188*, 425–431.
- (3) Few, G. A.; Rigby, M. Thermal pressure coefficient and internal pressure of 2, 2-dimethylpropane. *J. Phys. Chem.* **1975**, *79*, 1543–1546.
- (4) Fortune, G. C.; Malcolm, G. N. Thermal pressure coefficient and the entropy of melting at constant volume of isotactic polypropylene. *J. Phys. Chem.* **1967**, *71*, 876–879.
- (5) Marczak, W.; Kielek, K. Internal pressure in binary mixtures of methylpyridine isomers with H<sub>2</sub>O and D<sub>2</sub>O. *Int. J. Thermophys.* **2010**, *31*, 85–96.
- (6) Kumar, K. Estimates of internal pressure and molar refraction of imidazolium based ionic liquids as a function of temperature. *J. Solution Chem.* **2008**, *37*, 203–214.
- (7) Macdonald, D. D.; Hyne, J. B.; Swinton, F. L. Energy-volume coefficients of alcohol-water mixtures. *J. Am. Chem. Soc.* **1970**, *92*, 6355–6356.
- (8) Malcolm, G. N.; Ritchie, G. L. D. The thermal pressure coefficient and the entropy of melting at constant volume of polyethylene oxide. *J. Phys. Chem.* **1962**, *66*, 852–854.
- (9) Bolotnikov, M. F.; Neruchev, Y. A. Temperature dependence of the thermophysical properties of 1-chlorohexane, 1-iodohexane, 1-iodoheptane, and 1-chlorononane at saturation condition. *J. Chem. Eng. Data* **2004**, *49*, 202–207.
- (10) Lee, H. Y.; Liu, G. A generalized equation of state for liquid density calculation. *Fluid Phase Equilib.* **1995**, *108*, 15–25.
- (11) Goharshadi, E. K.; Morsali, A.; Abbaspour, M. New regularities and an equation of state for liquids. *Fluid Phase Equilib.* **2005**, *230*, 170–175.
- (12) Deiters, U. A new semiempirical equation of state for fluids. I: Derivation. *Chem. Eng. Sci.* **1981**, *36*, 1139–1146.
- (13) Song, Y.; Mason, E. A. Statistical-mechanical theory of a new analytical equation of state. *J. Chem. Phys.* **1989**, *91* (12), 7840–7853.
- (14) Smith, E. B. Equation of state of liquids at constant volume. *J. Chem. Phys.* **1962**, *36*, 1404–1405.
- (15) Moeini, V. J. A new regularity for internal pressure of dense fluids. *Phys. Chem. B* **2006**, *110*, 3271–3275.
- (16) Siepmann, J. I.; Schultz, N. E.; Ross, R. B. Pressure dependence of the hildebrand solubility parameter and the internal pressure: Monte carlo simulations for external pressures up to 300 MPa. *J. Phys. Chem. C* **2007**, *111*, 15634–15641.
- (17) Zeng, Z. Y.; Xu, Y. Y.; Li, X. S.; Li, Y. W. Empirical regularity of the thermal pressure coefficient for dense fluids. *Ind. Eng. Chem. Res.* **2010**, *49*, 7654–7659.
- (18) Zeng, Z. Y.; Xu, Y. Y.; Li, Y. W. Calculation of solubility parameter using perturbed-chain SAFT and cubic-plus-association equations of state. *Ind. Eng. Chem. Res.* **2008**, *47*, 9663–9669.
- (19) Parsafar, G. A.; Mason, E. A. Linear isotherms for dense fluids: A new regularity. *J. Phys. Chem.* **1993**, *97*, 9048–9053.
- (20) Diets, U. K.; Reuck, K. M. Guidelines for publication of equations of state: I. Pure fluids. *Fluid Phase Equilib.* **1999**, *161*, 205–219.
- (21) Tait, P. G. *The voyage of H. M. S. challenger*; Cambridge University Press: Cambridge, 1988; Vol. 2, Part 4.
- (22) Benedict, M.; Webb, G. B.; Rubin, L. C. An empirical equation for thermodynamic properties of light hydrocarbons and their mixtures I. Methane, ethane, propane and n-butane. *J. Chem. Phys.* **1940**, *8*, 334–345.
- (23) Setzmann, U.; Wagner, W. A new method for optimizing the structure of thermodynamic correlation equations. *Int. J. Thermophys.* **1989**, *10*, 1103–1126.
- (24) Song, Y.; Mason, E. A. Analytical equation of state for molecular fluids: Comparison with experimental data. *Phys. Rev. A* **1990**, *42*, 4749–4755.
- (25) van der Waals, J. D.; Kohnstamm, P. *Lehrbuch der Thermostatik*; Verlag von Johann Ambrosius Barth: Leipzig, 1927.
- (26) Redlich, O.; Kwong, J. N. S. On the thermodynamics of solutions. V. An equation of state. fugacities of gaseous solutions. *Chem. Rev.* **1949**, *44*, 233–244.
- (27) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid Phase Equilibria*, 3rd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1999.
- (28) Sados, R. J. *High Pressure Phase Behavior of Multicomponent Fluid Mixtures*; Elsevier: Amsterdam, 1992.
- (29) Sengers, J. M. H.L. Mean-field theories, their weaknesses and strength. *Fluid Phase Equilib.* **1999**, *158*, 3–17.
- (30) Sengers, J. V.; Sengers, J. M. H. L. Thermodynamic behavior of fluids near the critical point. *Annu. Rev. Phys. Chem.* **1986**, *37*, 189–222.
- (31) Anisimov, M. A.; Kiselev, S. B. Thermophysical properties of liquids and liquid solutions in the critical region. *Sov. Technol. Rev. B Therm. Phys.* **1992**, *3*, 1–119.
- (32) Sengers, J. M. H. L.; Sengers, J. V.; Raveche, H. J., Ed. *Perspectives in Statistical Physics*; North-Holland: Amsterdam, 1981.
- (33) Chen, Z. Y.; Abbaci, A.; Tang, S.; Sengers, J. V. Global thermodynamic behavior of fluids in the critical region. *Phys. Rev. A* **1990**, *42*, 4470–4484.
- (34) Abbaci, A.; Berrezeg, A. A thermodynamic equation of state for the critical region of ethylene. *Int. J. Thermophys.* **2004**, *25*, 739–752.
- (35) Gielen, H.; Jansoone, V.; Verbeke, O. Application of an empirical equation of state to the critical region of methane and argon. *J. Chem. Phys.* **1973**, *59*, 5763–5769.
- (36) Lee, Y.; Shin, M. S.; Yeo, J. K.; Kim, H. A crossover cubic equation of state near to and far from the critical region. *J. Chem. Thermodyn.* **2007**, *39*, 1257–1263.
- (37) Feyzi, F.; Seydi, M.; Alavi, F. Crossover Peng-Robinson equation of state with introduction of a new expression for the crossover function. *Fluid Phase Equilib.* **2010**, *293*, 251–260.

- (38) Wyczalkowska, A. K.; Sengers, J. V.; Anisimov, M. A. Critical fluctuations and the equation of state of van der Waals. *Phys. A* **2004**, *334*, 482–512.
- (39) Jiang, J.; Prausnitz, J. M. Equation of state for thermodynamic properties of chain fluids near-to and far-from the vapor–liquid critical region. *J. Chem. Phys.* **1999**, *111*, 5964–5974.
- (40) Leonhard, K. K.; Kraska, T. An equation of state describing the critical region: Extension to high pressure. *J. Supercrit. Fluids* **1999**, *16*, 1–10.
- (41) Chen, Z. Y.; Albright, P. C.; Sengers, J. V. Crossover from singular critical to regular classical thermodynamic behavior of fluids. *Phys. Rev. A* **1990**, *41*, 3161–3177.
- (42) Jin, G. X.; Tang, S.; Sengers, J. V. Global thermodynamic behavior of fluid mixtures in the critical region. *Phys. Rev. E* **1993**, *47*, 388–402.
- (43) Kiselev, S. B. Cubic crossover equation of state. *Fluid Phase Equilib.* **1998**, *147*, 7–23.
- (44) Kiselev, S. B.; Ely, J. F. Simplified crossover SAFT equation of state for pure fluids and fluid mixtures. *Fluid Phase Equilib.* **2000**, *174*, 93–113.
- (45) Patel, N. C.; Teja, A. S. A new cubic equation of state for fluids and fluid mixtures. *Chem. Eng. Sci.* **1982**, *37*, 463–473.
- (46) Peng, D. Y.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.
- (47) Parsafar, G. A.; Spohr, H. V.; Patey, G. N. An accurate equation of state for fluids and solids. *J. Phys. Chem. B* **2009**, *113*, 11977–11987.
- (48) Safdari, F.; Parsafar, G. A. Influence of quantum effect on deviation from linear isotherm regularity. *Sci. Iran. C* **2012**, *19*, 555–560.
- (49) Akbarzadeh, H.; Abroshan, H.; Farid Taherkhani, F.; Parsafar, G. A. Calculation of thermodynamic properties of Ni nanoclusters via selected equations of state based on molecular dynamics simulations. *Solid State Commun.* **2011**, *151*, 965–970.
- (50) Sadeghi, M.; Parsafar, G. A. Toward an equation of state for water inside carbon nanotubes. *J. Phys. Chem. B* **2012**, *116*, 4943–4951.
- (51) Levine, I. N. *Physical Chemistry*, sixth ed.; McGraw-Hill: New York, 2009.
- (52) Tegeler, Ch.; Span, R.; Wagner, W. A new equation of state for argon covering the fluid region for temperatures from the melting line to 700 K at pressures up to 1000 MPa. *J. Phys. Chem. Ref. Data* **1999**, *28*, 779–850.
- (53) Gilgen, R.; Kleinrahm, R.; Wagner, W. Measurement and correlation of the (pressure, density, temperature) relation of argon II. Saturated-liquid and saturated-vapour densities and vapour pressures along the entire coexistence curve. *J. Chem. Thermodyn.* **1994**, *26*, 399–413.
- (54) Nowak, P.; Kleinrahm, R.; Wagner, W. Measurement and correlation of the ( $p, \rho, T$ ) relation of nitrogen. II. Saturated-liquid and saturated-vapour densities and vapour pressures along the entire coexistence curve. *J. Chem. Thermodyn.* **1997**, *29*, 1157–1174.
- (55) Levelt Sengers, J. M. H.; Straub, J.; Watanabe, K.; Hill, P. G. Assessment of critical parameter values for H<sub>2</sub>O and D<sub>2</sub>O. *J. Phys. Chem. Ref. Data* **1985**, *14*, 193–207.
- (56) Kleinrahm, R.; Wagner, W. Measurement and correlation of the equilibrium liquid and vapour densities and the vapour pressure along the coexistence curve of methane. *J. Chem. Thermodyn.* **1986**, *18*, 739–760.
- (57) Span, R.; Lemmon, E. W.; Jacobsen, R. T.; Wagner, W.; Yokozeki, A. A reference equation of state for the thermodynamic properties of nitrogen for temperatures from 63.151 to 1000 K and pressures to 2200 MPa. *J. Phys. Chem. Ref. Data* **2000**, *29* (6), 1361–1433.
- (58) Wagner, W.; Pruss, A. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *J. Phys. Chem. Ref. Data* **2002**, *31* (2), 387–535.
- (59) Setzmann, U.; Wagner, W. A new equation of state and tables of thermodynamic properties for methane covering the range from the melting line to 625 K at pressures up to 100 MPa. *J. Phys. Chem. Ref. Data* **1991**, *20* (6), 1061–1151.
- (60) Wei, Y. S.; Sadus, R. G. Equations of state for the calculation of fluid-phase equilibria. *AIChE J.* **2000**, *46*, 169–196.
- (61) Tian, J.; Gui, Y.; Mulero, A. New closed virial equation of state for hard-sphere fluids. *J. Phys. Chem. B* **2010**, *114*, 13399–13402.
- (62) Clisby, N.; McCoy, B. M. Ninth and tenth order virial coefficients for hard spheres in D dimensions. *J. Stat. Phys.* **2006**, *122*, 15–57.
- (63) Stewart, R. B.; Jacobsen, R. T.; Wanger, W. Thermodynamic properties of oxygen from the triple point to 300 K with pressures to 80 MPa. *J. Phys. Chem. Ref. Data* **1991**, *20* (5), 917–1051.
- (64) Pai, S. J.; Bae, Y. C. Understanding physical properties of hydrocarbon polymers using an equation of state developed from semi soft core potential function. *Fluid Phase Equilib.* **2012**, *317*, 15–24.
- (65) Shokouhi, M.; Parsafar, G. A. A new equation of state derived by the statistical mechanical perturbation theory. *Fluid Phase Equilib.* **2008**, *264*, 1–11.
- (66) Parsafar, G. A.; Khanpour, M.; Mohammadi, A. A. Calculation of equilibrium and transport properties using modified hard-core potential models. *Chem. Phys.* **2006**, *326*, 527–534.
- (67) Carnahan, N. F.; Starling, K. E. Equation of state for nonattracting Rigid Spheres. *J. Chem. Phys.* **1969**, *51*, 635–636.
- (68) Boublik, T. Statistical thermodynamics of nonspherical molecule fluids. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 1038–1041.
- (69) National Institute of Standards and Technology (NIST) Database 2012, <http://webbook.nist.gov/chemistry/fluid>.
- (70) Smith, B. D.; Srivastava, R. *Thermodynamic Data for Pure Compounds*; Elsevier: Amsterdam, 1986.
- (71) Lide, D. R., Ed.-in-Chief. *CRC Handbook of Chemistry and Physics*, 87th ed.; Taylor and Francis: Boca Raton, FL, 2007.
- (72) Dicko, M.; Coquelet, C. Application of a new crossover treatment to a generalized cubic equation of state. *Fluid Phase Equilib.* **2011**, *302*, 241–248.