

## A cubic hard-core equation of state

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### Abstract

In this work, a new method to determine a suitable repulsive term for cubic equations of state is introduced. Based on this method and by using a simplified molecular theory of hard-core fluids, a new two constant parameter cubic equation of state is presented. The proposed equation of state is applied for PVT and VLE calculations of different pure fluids and fluid mixtures. The results are compared with those obtained by two commonly used cubic equations of state. The comparisons indicate that the new equation of state yields better results.

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*Keywords:* Cubic equation of state; Hard-core fluids; PVT and VLE calculations; Repulsive and attractive terms in EOS

### 1. Introduction

Recent developments in phase behavior modeling of fluids indicate that more serious considerations must be given to basic studies to produce simple theoretical and more accurate equations of state for the representation of both volumetric and equilibrium properties of fluids used in chemical process design.

During the past 20 years great interest has developed in the properties of fluids and fluid mixtures [1,2]. This has evolved from several sources, notably, optimum design and industrial operations in gas and oil industry [3,4]. Therefore, theoretical and semi-empirical equations of state for accurate prediction of phase behavior as well as thermodynamic properties of pure fluids and mixtures of fluids have been introduced. The applicability of existing equations of state is limited to specific temperature and pressure ranges [2,5]. Research and investigations are in progress to find a new equation of state for all substances in all ranges of temperature and pressure. There has been considerable progress in the development of equations of state based on the molecular theory of statistical mechanics, however, due to the many

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applications of cubic equations of state, it is still worth while to make improvements on empirical and semi-empirical equations of state of industrial interest.

Although, the van der Waals (vdW) family equations of state such as the well-known cubic Redlich–Kwong (RK), Soave–Redlich–Kwong (SRK), and Peng–Robinson (PR) equations of state and their modifications, predict poor volumetric behavior [3,6,7], the cubic molecular based equations of state are still used for engineering calculations [5,7,8–13]. The poor volumetric behavior of vdW equations of state may be removed by considering the importance of the role of repulsive forces in the behavior of fluids [1,3,14]. In this manner, the molecular interactions can be considered as two separated repulsive and attractive effects. Therefore, by choosing a suitable repulsive term for the cubic equations of state a simple theoretical cubic equation of state can be derived [1,5,15–18].

There are various methods based on a molecular approach to obtain an equation of state and its parameters [6,14,19,20]. In this work, we introduce a new method based on deriving the repulsive term of the cubic equations of state and then, by using a general form for the attractive term, a two constant cubic equation of state is proposed. The proposed equation has been modified by a simple functional form for its attractive and repulsive parameters [ $a(T)$  and  $b(T)$ ].

The proposed equation of state is applied to vapor pressure and saturated densities calculations of different pure fluids. Then, the proposed equation is extended to mixtures and the results are compared with those obtained from the equations of state frequently used for thermodynamic and fluid phase equilibrium calculations [10–13]. The comparisons indicate that the proposed equation of state is quite suitable for property predictions of gas and liquid systems of interest in the oil and gas industries. The major advantage of this equation is the sound theoretical basis used in deriving the repulsive term [1,8,9], and this makes it more suitable for extrapolation purposes compared with the similar empirical equations.

## 2. Theory

According to the concept of perturbation theory of statistical mechanics, the compressibility factor,  $Z$ , is presented as

$$Z = Z_0 + Z_1 + Z_2 + \dots \quad (1)$$

where  $Z_0$  is the hard-sphere compressibility factor considered as the unperturbed term and  $Z_1$  and  $Z_2$ , etc., are the corrections to  $Z_0$ . As the successive corrections become increasingly less significant, the exact solution of  $Z$  depends on the accurate solution of the unperturbed hard-sphere compressibility factor term,  $Z_0$  [17,18].

The first term in Eq. (1), which can be considered as the repulsive term is given by van der Waals [21] as

$$Z_{\text{rep}} = \frac{1}{v - b} \quad (2)$$

The main defect in vdW type equations of state such as the RK, SRK and PR equations [10–13], is the use of the term  $(1/(v - b))$  to represent the repulsive term. In fact, molecular dynamic results show that Eq. (2) is accurate up to a packing fraction,  $y = b/(4v) = 0.1$ .

The Carnahan–Starling (CS) equation of state [17] is an accurate equation of state for hard-spheres:

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

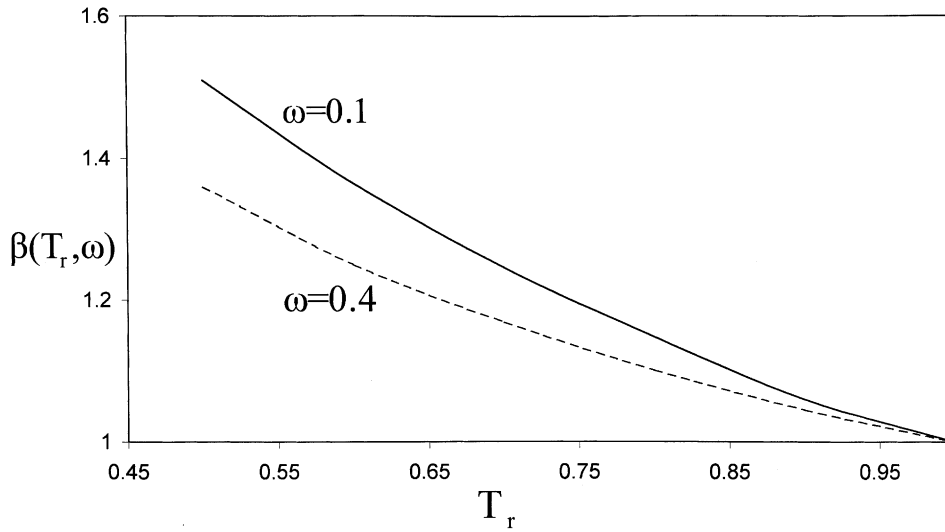


Fig. 1. The variation of  $[\beta(T_r, \omega)]$  versus temperature ( $T_r$ ) for various acentric factors ( $\omega$ ).

This equation can be used as the repulsive term instead of  $1/(v - b)$  in the vdW type equations of state. However, the resulting equation of state will not be cubic. So, to retain the cubic form we introduced an exact repulsive term at a limited packing fraction,  $y$ , according to following procedure:

1. We define a hard-core equation of state in terms of packing fraction,  $y$ , of the following form [1]:

$$Z_{\text{rep}} = \frac{1 + \theta y}{1 - \beta y} \tag{4}$$

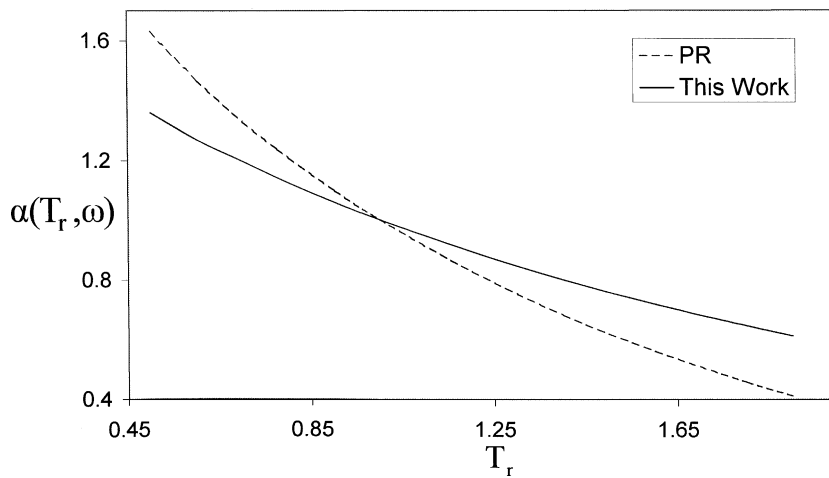


Fig. 2. The variation of  $[\alpha(T_r, \omega)]$  versus temperature ( $T_r$ ) for  $\omega = 0.4$  is compared with the temperature functional form of the attractive term of the PR equation of state.

By choosing  $\theta$  and  $\beta$  we can present an accurate hard-core equation of state in a limited range of packing fractions,  $0 < y < y^*$ . Where  $y^*$  represents the upper limit of the packing fraction. Its significance becomes clear later.

2. The above hard-core equation of state can be used as the repulsive term of a new cubic equation of state. Therefore, we introduce the new cubic equation of state as [2].

$$Z = \frac{v + \theta b}{v - \beta b} - \frac{a}{[RT^{n+1}(v + \gamma\beta b)]} \quad (5)$$

Table 1  
Relative error in vapor pressure calculations

Components	No. of data	Range of $T_r$	%AAD <sup>a</sup>			Reference
			PR	SRK	New	
CH <sub>4</sub>	17	0.53–0.95	1.36	2.36	0.71	[23]
C <sub>2</sub> H <sub>6</sub>	16	0.46–0.95	1.65	2.03	0.58	[23]
C <sub>3</sub> H <sub>8</sub>	18	0.51–0.97	0.84	1.27	0.58	[23]
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	20	0.52–0.96	0.60	1.66	0.93	[24]
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	14	0.64–0.96	0.85	1.02	0.95	[24]
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	15	0.64–0.97	0.42	1.05	0.73	[24]
<i>i</i> -C <sub>5</sub> H <sub>12</sub>	18	0.53–0.94	1.05	1.56	1.21	[24]
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	10	0.53–0.97	1.13	1.84	1.41	[24]
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	11	0.56–0.93	1.37	1.63	1.43	[25]
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	14	0.49–0.95	2.33	1.61	1.79	[25]
<i>n</i> -C <sub>9</sub> H <sub>20</sub>	14	0.51–0.94	2.75	2.02	1.80	[25]
<i>n</i> -C <sub>10</sub> H <sub>22</sub>	13	0.55–0.94	2.20	2.07	1.69	[26]
C <sub>6</sub> H <sub>6</sub>	12	0.53–0.93	1.30	0.72	0.82	[26]
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	13	0.47–0.88	1.55	1.53	1.02	[26]
C <sub>2</sub> H <sub>4</sub>	16	0.42–0.96	2.60	1.83	1.53	[27]
C <sub>2</sub> H <sub>2</sub>	12	0.62–0.94	1.42	2.20	1.70	[23]
C <sub>3</sub> H <sub>6</sub>	11	0.44–0.99	2.11	1.79	0.71	[28]
CH <sub>3</sub> Cl	16	0.51–0.95	2.38	1.97	1.78	[26]
C <sub>2</sub> H <sub>5</sub> Cl	18	0.48–0.96	1.58	1.32	0.72	[26]
1,3-Butadiene	14	0.50–0.86	1.14	2.05	0.87	[29]
H <sub>2</sub>	10	0.42–0.96	4.40	8.17	5.06	[26]
SO <sub>2</sub>	19	0.49–0.96	2.58	4.08	3.67	[24]
CO <sub>2</sub>	14	0.71–0.95	0.70	0.41	0.41	[23]
N <sub>2</sub>	14	0.50–0.95	1.54	1.73	1.28	[23]
O <sub>2</sub>	17	0.45–0.97	1.79	2.15	1.42	[30]
CO	24	0.53–0.98	2.10	0.62	1.70	[23]
CF <sub>4</sub>	10	0.57–0.97	1.06	0.85	0.82	[26]
H <sub>2</sub> S	15	0.57–0.98	2.22	1.60	1.55	[24]
F <sub>2</sub>	8	0.49–0.97	0.44	2.62	0.97	[26]
Cl <sub>2</sub>	17	0.56–0.96	2.27	3.25	3.18	[26]
Grand average			1.65	1.97	1.43	

$$^a \text{ \%AAD} = \frac{1}{N} \sum_{i=1}^N \left| \frac{P_{\text{calculated}} - P_{\text{experimental}}}{P_{\text{experimental}}} \right| \times 100.$$

where  $n$  and  $\gamma$  have arbitrary values. By considering Eq. (4) as the repulsive term with the purpose to retain the cubic form in the derived equation of state, it is necessary to have a simple general attractive term (represented by the second term of Eq. (5)). This general attractive term can be reduced to the attractive term of the RK equation of state by choosing  $n = 0.5$ ,  $\gamma = \beta = 1$ .

- By imposing the critical constrains on Eq. (5), the attractive and repulsive parameters ( $a$  and  $b$ ) can be determined.
- By considering the triple point and critical density of fluids, the maximum packing fractions for different fluids are determined [1]. The obtained values will be compared with  $y^*$ . As a result the maximum packing fraction must be less than  $y^*$ . Otherwise, steps 1–4 are repeated.

Table 2  
Relative error in liquid density calculations

Components	No. of data	Range of $T_r$	%AAD <sup>a</sup>			Reference
			PR	SRK	New	
CH <sub>4</sub>	17	0.53–0.95	8.13	4.42	2.11	[23]
C <sub>2</sub> H <sub>6</sub>	16	0.46–0.95	6.25	6.82	2.88	[23]
C <sub>3</sub> H <sub>8</sub>	18	0.51–0.97	5.39	9.47	3.12	[23]
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	20	0.52–0.96	4.38	10.80	3.13	[24]
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	14	0.64–0.96	4.38	10.45	3.60	[24]
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	15	0.64–0.97	3.97	14.44	4.26	[24]
<i>i</i> -C <sub>5</sub> H <sub>12</sub>	18	0.53–0.94	3.70	12.52	3.03	[24]
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	10	0.53–0.97	3.31	16.36	3.70	[24]
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	11	0.56–0.93	2.07	15.50	3.17	[25]
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	14	0.49–0.95	5.30	19.01	3.34	[25]
<i>n</i> -C <sub>9</sub> H <sub>20</sub>	14	0.51–0.94	5.30	19.02	3.30	[25]
<i>n</i> -C <sub>10</sub> H <sub>22</sub>	13	0.55–0.94	8.17	22.32	3.86	[26]
C <sub>6</sub> H <sub>6</sub>	12	0.53–0.93	2.78	12.14	2.23	[26]
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	13	0.47–0.88	2.22	15.15	2.93	[26]
C <sub>2</sub> H <sub>4</sub>	16	0.42–0.96	7.30	5.20	3.56	[27]
C <sub>2</sub> H <sub>2</sub>	12	0.62–0.94	4.44	12.54	3.80	[23]
C <sub>3</sub> H <sub>6</sub>	11	0.44–0.99	5.58	7.30	3.23	[28]
CH <sub>3</sub> Cl	16	0.51–0.95	4.40	12.38	3.98	[26]
C <sub>2</sub> H <sub>5</sub> Cl	18	0.48–0.96	0.83	12.01	2.60	[26]
1,3-Butadiene	14	0.50–0.86	2.93	9.89	1.74	[29]
H <sub>2</sub>	10	0.42–0.96	17.43	9.06	6.19	[26]
SO <sub>2</sub>	19	0.49–0.96	2.17	14.00	2.83	[24]
CO <sub>2</sub>	14	0.71–0.95	3.65	11.48	1.19	[23]
N <sub>2</sub>	14	0.50–0.95	9.10	3.38	2.78	[23]
O <sub>2</sub>	17	0.45–0.97	8.66	4.00	3.40	[30]
CO	24	0.53–0.98	8.84	3.66	2.75	[23]
CF <sub>4</sub>	10	0.57–0.97	5.79	8.69	4.27	[26]
H <sub>2</sub> S	15	0.57–0.98	5.70	7.33	2.26	[24]
F <sub>2</sub>	8	0.49–0.97	8.86	4.60	3.31	[26]
Cl <sub>2</sub>	17	0.56–0.96	4.41	10.32	2.85	[26]
Grand average			5.52	10.81	3.18	

$$^a \text{ \%AAD} = \frac{1}{N} \sum_{i=1}^N \left| \frac{\rho_{\text{calculated}} - \rho_{\text{experimental}}}{\rho_{\text{experimental}}} \right| \times 100.$$

This method is used to obtain a hard-core equation of state in a limited range of packing fractions and the resulting equation can be considered as the repulsive term of simple cubic equations of state.

On the other hand, the attractive term will be adjusted to obtain the best values of the coefficients  $\theta$  and  $\beta$  in the repulsive term. In this manner, the hard-sphere compressibility factor can be used as a suitable simple reference term in the perturbation theory to deriving an equation of state, the application of this reference term as the most exact one is questionable. Therefore, the accuracy of the perturbation theory is based on the following factors:

1. The best choice of the unperturbed or reference term (in this work, hard-sphere term).
2. The most suitable choice of the perturbed term (attractive term).

Table 3  
Relative error in saturated vapor density calculations

Components	No. of data	Range of $T_r$	%AAD <sup>a</sup>			Reference
			PR	SRK	New	
CH <sub>4</sub>	17	0.53–0.95	2.44	2.48	2.02	[23]
C <sub>2</sub> H <sub>6</sub>	16	0.46–0.95	1.65	1.94	1.43	[23]
C <sub>3</sub> H <sub>8</sub>	18	0.51–0.97	1.40	1.43	1.44	[23]
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	20	0.52–0.96	1.11	1.67	1.72	[24]
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	14	0.64–0.96	0.94	0.88	1.37	[24]
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	15	0.64–0.97	1.30	0.84	1.99	[24]
<i>i</i> -C <sub>5</sub> H <sub>12</sub>	18	0.53–0.94	1.38	2.13	2.00	[24]
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	10	0.53–0.97	1.60	2.40	2.00	[24]
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	11	0.56–0.93	1.20	0.40	3.11	[25]
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	14	0.49–0.95	2.61	2.18	2.03	[25]
<i>n</i> -C <sub>9</sub> H <sub>20</sub>	14	0.51–0.94	6.83	6.30	4.88	[25]
<i>n</i> -C <sub>10</sub> H <sub>22</sub>	13	0.55–0.94	1.88	2.73	1.63	[26]
C <sub>6</sub> H <sub>6</sub>	12	0.53–0.93	1.50	2.81	1.30	[26]
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	13	0.47–0.88	2.98	1.96	2.45	[26]
C <sub>2</sub> H <sub>4</sub>	16	0.42–0.96	2.69	1.85	2.20	[27]
C <sub>2</sub> H <sub>2</sub>	12	0.62–0.94	1.30	1.77	1.29	[23]
C <sub>3</sub> H <sub>6</sub>	11	0.44–0.99	1.79	2.35	0.91	[28]
CH <sub>3</sub> Cl	16	0.51–0.95	5.64	3.26	5.52	[26]
C <sub>2</sub> H <sub>5</sub> Cl	18	0.48–0.96	4.67	2.25	4.01	[26]
1,3-Butadiene	14	0.50–0.86	1.05	1.87	1.27	[29]
H <sub>2</sub>	10	0.42–0.96	12.20	15.02	6.80	[26]
SO <sub>2</sub>	19	0.49–0.96	3.37	5.43	4.36	[24]
CO <sub>2</sub>	14	0.71–0.95	1.61	1.70	3.90	[23]
N <sub>2</sub>	14	0.50–0.95	3.81	2.74	3.50	[23]
O <sub>2</sub>	17	0.45–0.97	2.34	2.50	2.13	[30]
CO	24	0.53–0.98	3.12	2.31	2.27	[23]
CF <sub>4</sub>	10	0.57–0.97	1.66	1.78	1.30	[26]
H <sub>2</sub> S	15	0.57–0.98	4.82	3.13	5.12	[24]
F <sub>2</sub>	8	0.49–0.97	1.44	2.92	1.77	[26]
Cl <sub>2</sub>	17	0.56–0.96	2.42	3.38	2.95	[26]
Grand average			2.76	2.82	2.66	

$$^a \text{ \%AAD} = \frac{1}{N} \sum_{i=1}^N \left| \frac{\rho_{\text{calculated}} - \rho_{\text{experimental}}}{\rho_{\text{experimental}}} \right| \times 100.$$

Table 4  
Relative error in the calculated pressure and vapor phase composition for various mixtures

Systems (1) + (2)	No. of data	%P error		%Y error		$K_{ij}$		Reference
		PR	New	PR	New	PR	New	
CH <sub>4</sub> + CO <sub>2</sub>	9	1.11	2.13	2.86	2.38	0.102	0.022	[39]
CH <sub>4</sub> + <i>n</i> -C <sub>10</sub> H <sub>22</sub>	6	1.92	1.24	3.65	2.65	0.150	−0.394	[38]
CH <sub>4</sub> + C <sub>7</sub> H <sub>8</sub>	8	5.11	3.84	2.96	2.31	0.087	−0.213	[38]
CH <sub>4</sub> + H <sub>2</sub>	15	1.71	1.66	1.79	1.61	0.189	−0.703	[35]
CH <sub>4</sub> + C <sub>6</sub> H <sub>6</sub>	9	5.96	5.59	2.99	2.96	−0.081	−0.076	[41]
CO <sub>2</sub> + <i>n</i> -C <sub>4</sub> H <sub>10</sub>	13	1.10	1.82	0.90	1.36	0.163	0.102	[36]
CO <sub>2</sub> + <i>n</i> -C <sub>5</sub> H <sub>12</sub>	14	0.76	1.13	2.26	3.94	0.120	0.061	[37]
CO <sub>2</sub> + <i>n</i> -C <sub>6</sub> H <sub>14</sub>	10	2.15	1.15	0.32	0.56	0.125	0.067	[44]
CO <sub>2</sub> + C <sub>2</sub> H <sub>4</sub>	15	0.34	0.32	0.68	0.83	0.052	0.049	[42]
CO <sub>2</sub> + C <sub>7</sub> H <sub>8</sub>	12	6.96	3.56	0.81	0.47	0.111	0.044	[34]
CO <sub>2</sub> + <i>n</i> -C <sub>7</sub> H <sub>16</sub>	23	2.03	2.96	0.60	0.59	0.108	0.037	[44]
CO <sub>2</sub> + C <sub>6</sub> H <sub>6</sub>	15	4.56	3.48	0.34	0.48	0.095	0.065	[43]
N <sub>2</sub> + <i>i</i> -C <sub>4</sub> H <sub>10</sub>	11	3.77	2.31	0.70	0.55	0.102	−0.086	[40]
H <sub>2</sub> + CF <sub>4</sub>	5	4.59	3.80	3.29	2.60	0.245	−0.507	[33]
H <sub>2</sub> + R-13	6	1.19	0.99	2.95	1.27	0.239	−0.916	[33]
R-13 + <i>i</i> -C <sub>4</sub> H <sub>10</sub>	18	0.57	1.03	1.03	1.11	0.067	0.054	[32]
R-13 + <i>n</i> -C <sub>4</sub> H <sub>10</sub>	17	0.37	0.94	1.07	2.25	0.075	0.036	[32]
C <sub>7</sub> H <sub>8</sub> + <i>n</i> -C <sub>10</sub> H <sub>22</sub>	10	2.15	1.81	3.45	2.24	−0.021	−0.018	[31]
Grand average		2.58	2.20	1.81	1.67			

In the present work, a simple and accurate hard-sphere compressibility factor has been considered as the unperturbed term, and the successive terms are replaced by a simple general term. We believe that for any unperturbed term, a perturbed term can be found as the best replacement of the correction terms in the perturbation theory. The consistency of the unperturbed and perturbed terms is referred to as the “coupling effect”. The best combination of the unperturbed and perturbed terms may compensate the errors involved in the approximations. On the other hand, it is possible to obtain the best results from a cubic equation of state by coupling of  $Z_{rep}$  with a proper  $Z_{att}$  [22].

Table 5  
Relative error in density calculations of heavy hydrocarbons

Components	Range of $T_r$	Range of $P$ (atm)	%AAD			Reference
			PR	SRK	New	
<i>n</i> -C <sub>9</sub> H <sub>20</sub>	0.50–0.96	1–100	3.65	16.82	4.25	[45]
<i>n</i> -C <sub>11</sub> H <sub>24</sub>	0.47–0.89	1–100	5.91	18.44	5.05	[45]
<i>n</i> -C <sub>13</sub> H <sub>28</sub>	0.45–0.85	1–100	8.11	21.35	5.48	[45]
<i>n</i> -C <sub>17</sub> H <sub>36</sub>	0.44–0.78	1–100	18.08	32.72	6.21	[45]
<i>n</i> -C <sub>20</sub> H <sub>42</sub>	0.48–0.75	1–100	22.31	37.22	6.48	[45]
Grand average			11.47	25.31	5.49	

Based on the above procedure the MMM equation of state have been presented [1,2]. The PVT and VLE calculations using the MMM equation indicated its superiority over vdW based equations of state [1,4].

In this work, for volumetric and phase equilibria calculations especially for dense fluids, a new form of the MMM equation of state is introduced as [1,2]:

$$Z = \left[ \frac{(v + \alpha b)}{(v - b)} \right] - \frac{a}{[RT^{3/2}(v + \gamma b)]} \quad (6)$$

According to the original the MMM equation of state,  $\alpha = 1.3191$ ,  $b = \beta b$  and  $\gamma = 1$ . By considering the role of repulsive forces in determining the structure of fluids and the concept of “coupling effect” [22], the weight of the repulsive term in the original MMM equation of state can be increased by considering  $\gamma > 1$ . Therefore, we proposed that  $\gamma = N\alpha$ , where  $N = 1, 2, 3, \dots$ . It is worth noting that since  $\alpha > 1$ ,  $\gamma > 1$ .

The new cubic hard-core equation of state is presented in the following form:

$$Z = \left[ \frac{v + ab}{v - b} \right] - \frac{a}{[RT^{3/2}(v + N\alpha b)]} \quad (7)$$

There are two constrains for the selection of the value of  $N$ .

1. The maximum packing fraction for different fluids according to Eq. (7) must be less than  $y^* = 0.35$  [1].
2. The constant critical compressibility factor ( $Z_c$ ) must match the average critical compressibility factor of real fluids (about 0.3).

By the above considerations, we choose;  $N = 2$  and by imposing the critical point constrains, we can derive the following expressions:

$$a_c = 0.47312 \left( \frac{R^2 T_c^{2.5}}{P_c} \right) \quad (8)$$

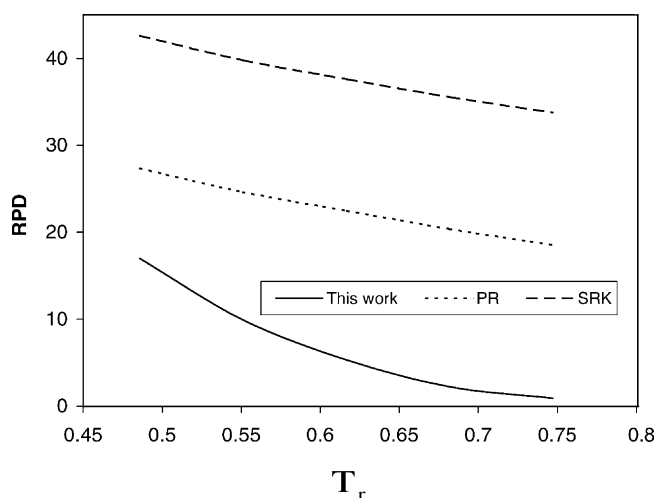


Fig. 3. The relative percent deviations (RPD), of  $n\text{-C}_{20}\text{H}_{42}$  liquid density versus the reduced temperature,  $T_r$ , at  $P = 1$  atm.

$$b_c = 0.04616 \left( \frac{RT_c}{P_c} \right) \tag{9}$$

$$Z_c = 0.308 \tag{10}$$

The critical compressibility factor of the proposed equation of state ( $Z_c = 0.308$ ) is near the average value for critical compressibility factor of real simple fluids and, as it is expected for an equation of state with two constant parameters,  $Z_c$  is a constant regardless of the kind of fluid. This justifies our choice of  $N = 2$ .

The accurate prediction of vapor pressures and liquid densities of fluids, by two constant parameter cubic equations of state can be enhanced by choosing the appropriate temperature and acentric factor functionality for parameters “ $a$ ” and “ $b$ ”, in the following form [11,13,19]:

$$a = a_c[a(T_r, \omega)] \quad \text{and} \quad b = b_c[\beta(T_r, \omega)] \tag{11}$$

There are a number of theoretical and empirical temperature functions presented for the attractive and repulsive parameters ( $a$  and  $b$ ) [4]. In this work, we have considered the most simple and common temperature functions for “ $a$ ” and “ $b$ ”. The simple temperature function for parameter “ $a$ ” is in the following form [11]:

$$a = a_c[1 + m(1 - T_r^{0.5})]^2 \tag{12}$$

where  $m$  is a linear function of the acentric factor,  $\omega$ .

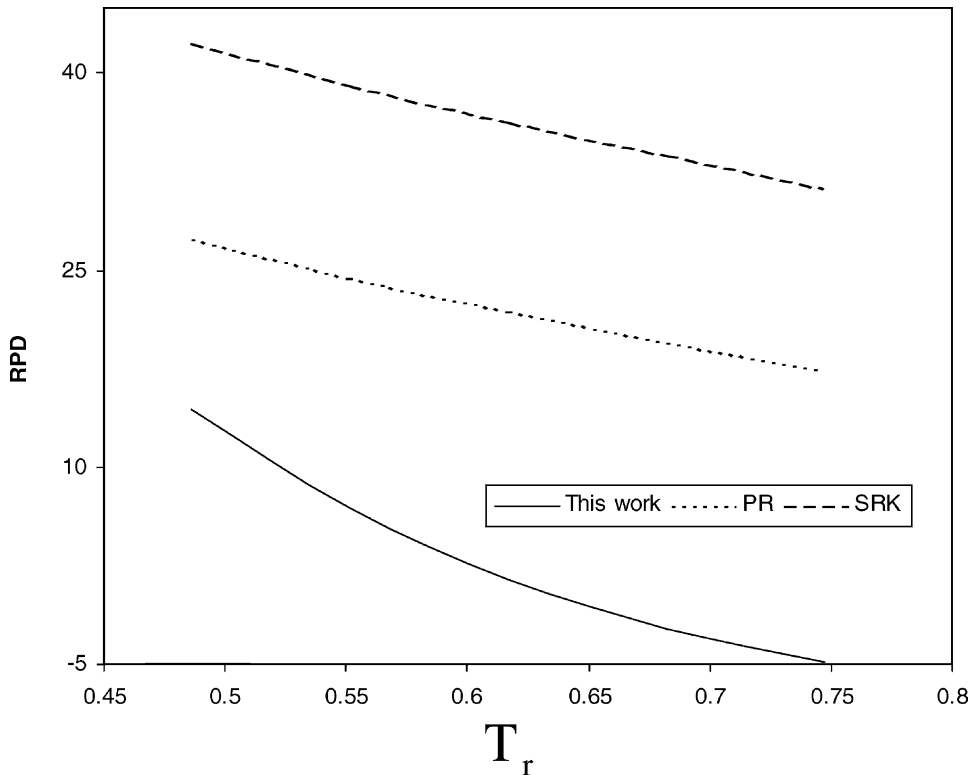


Fig. 4. The relative percent deviations (RPD), of  $n\text{-C}_{20}\text{H}_{42}$  liquid density versus the reduced temperature,  $T_r$ , at  $P = 100$  atm.

However, for the accurate prediction of saturated liquid densities of fluids, we have presented a similar expression for the repulsive parameter “ $b$ ” as

$$b = b_c[1 + n_1(1 - T_r^{0.5}) + n_2(1 - T_r^{0.75})]^2 \quad \text{for } T_r < 1 \quad (13)$$

Our calculations indicate that in a limited range of temperature ( $0.45 < T_r < 1$ ), the numerical values of the temperature function represented by Eq. (13) are matched with the numerical values of theoretical models [4]. After, correcting the parameter “ $b$ ” as  $b = b_c [\beta(T_r, \omega)]$  the upper limit of  $y^*$  has been calculated for a number fluids [1]. According to these calculations  $y^* < 0.35$  so, the maximum packing fraction is in the allowable range. On the other hand, after the correction,  $b = b_c[\beta(T_r, \omega)]$ , the repulsive term of the proposed equation of state can predict the hard-sphere properties in the limited range of packing fraction ( $y^* < 0.35$ ).

To obtain  $m$ ,  $n_1$  and  $n_2$ , in Eqs. (12) and (13), we have used the experimental data of vapor pressures and liquid densities of only three substances (methane, propane and octane) and the general form of them is presented as

$$m = 0.32 + 0.64\omega \quad (14)$$

$$n_1 = 3.270572 - 6.4127\omega + 10.6821\omega^2 \quad (15)$$

$$n_2 = -1.72192 + 3.85288\omega - 7.202286\omega^2 \quad (16)$$

The presented functional form for “ $a$ ” and “ $b$ ”, expressed by Eqs. (12) and (13), satisfies the basic

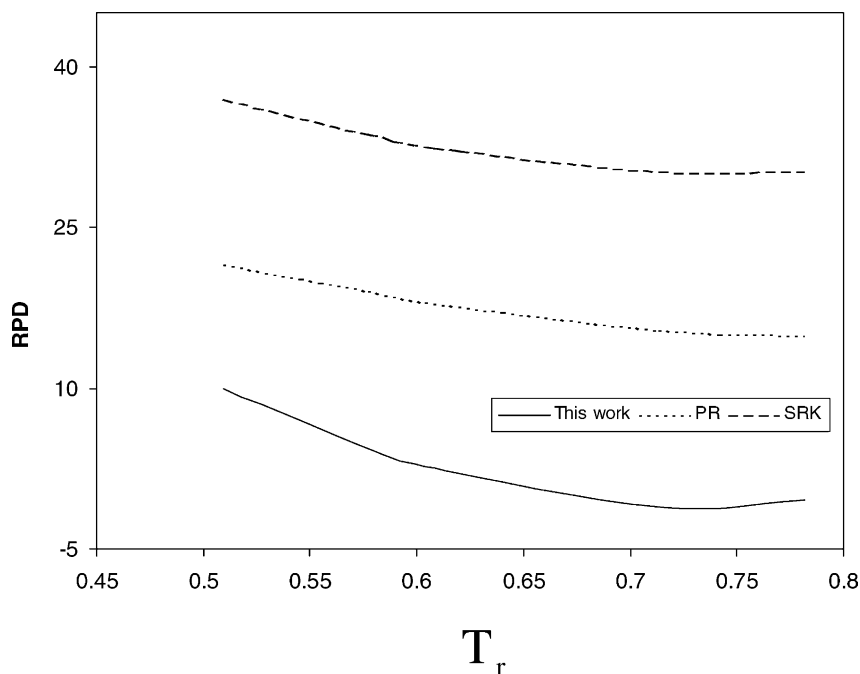


Fig. 5. The relative percent deviations (RPD), of  $n\text{-C}_{17}\text{H}_{36}$  liquid density versus the reduced temperature,  $T_r$ , at  $P = 1$  atm.

theoretical conditions for these functions at the critical point, i.e.

$$[\alpha(T_r, \omega)] = [\beta(T_r, \omega)] \rightarrow 1 \text{ at } T_r \rightarrow 1.$$

In Fig. 1 the variation of  $[\beta(T_r, \omega)]$  versus temperature ( $T_r$ ) for the various acentric factors is shown. As it is expected based on the variational and perturbation molecular theories of fluids  $[\beta(T_r, \omega)]$  is a decreasing function of temperature [4]. It can also be inferred from the form of the equation of state, Eq. (7), that when the temperature goes to infinity, the attractive term of the equation of state,  $a/[RT^{3/2}(v + N\alpha b)]$ , must go zero. The form of  $\alpha(T_r, \omega)$  considered in this work satisfy this requirement.

In Fig. 2 the variation of  $[\alpha(T_r, \omega)]$  versus temperature ( $T_r$ ) for  $\omega = 0.4$  is compared with the temperature functional form of the attractive term of the PR equation of state.

Now, the proposed equation of state is applied to calculate VLE and PVT behavior of various pure fluids and mixtures of fluids.

### 3. Results

Vapor pressures and saturated liquid and vapor densities of pure fluids calculated by the proposed equation are presented respectively in Tables 1–3. Also in these tables the results of calculations are compared with those obtained by the SRK and PR equations of state. The SRK and PR equations of state are the most commonly used equations for engineering design calculations, especially in oil and gas industries. According to these tables the proposed equation of state is more accurate than the SRK and PR equations.

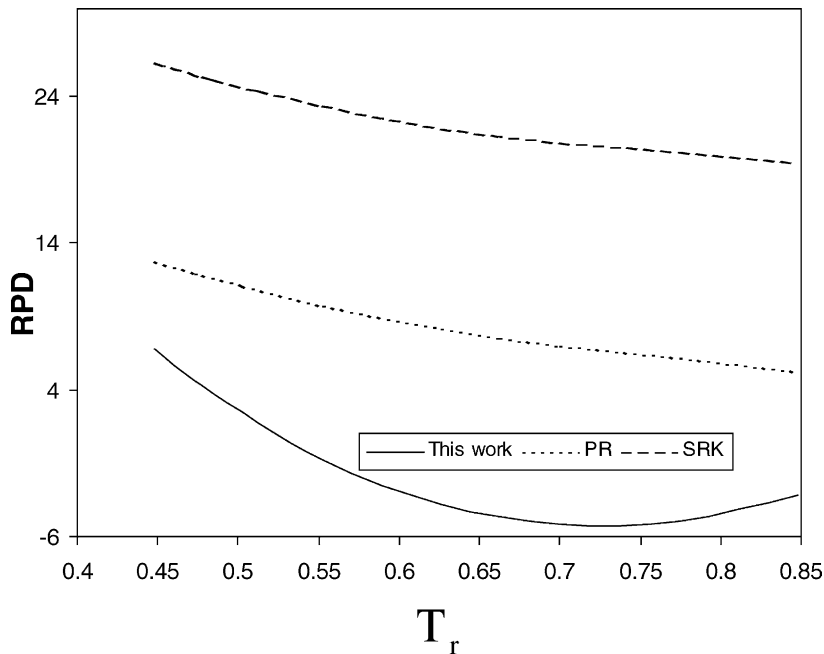


Fig. 6. The relative percent deviations (RPD), of  $n\text{-C}_{13}\text{H}_{28}$  liquid density versus the reduced temperature,  $T_r$ , at  $P = 1$  atm.

The proposed equation of state is applied for binary VLE calculations. The following conventional mixing rules for two parameter equations of state are used.

$$\begin{aligned} b &= \sum_i x_i b_i \\ a &= \sum_i \sum_j x_i x_j a_{ij} \\ a_{ij} &= (1 - k_{ij})(a_i a_j)^{1/2} \end{aligned} \quad (17)$$

Because, for the considered binary systems, our calculations indicate the superiority of the PR equation over the SRK equation for VLE calculations, we only compare the results obtained by the proposed equation of state with those from the PR equation of state. The comparisons presented in Table 4 show that the proposed equation of state is superior to the PR equation.

The proposed equation of state is applied for density calculations of heavy hydrocarbons at the different temperatures and pressures. The results are compared with those obtained by using the SRK and PR equations of state. The results, reported in Table 5, indicates that the overall performance of the proposed equation of state is better than the SRK and PR equations of state. Also the comparisons presented in Figs. 3–6 show the superiority of the proposed equation of state.

#### 4. Conclusion

A modified cubic hard-core equation of state is proposed. The thermodynamic property calculations and comparisons of the results with the popular cubic equations of state, such as SRK and PR, indicate that the proposed equation has a acceptable performance for property predictions of pure fluids and mixtures of fluids. One major advantage of the proposed equation is its sound theoretical basis in the coupling of its repulsive and attractive terms and this makes it more suitable for extrapolation purposes compared with the empirical equations of state.

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