A Simple Cubic Equation of State for Hydrocarbons and other Compounds


ABSTRACT

A new simple two-constant cubic equations of state for hydrocarbons, hydrocarbon mixtures, and other non-associating compounds is introduced. This equation of state is based on the statistical mechanical information available for the repulsive thermodynamic functions and the phenomenological knowledge of the attractive intermolecular potential tail contributions to the thermodynamic properties. This new two-constant parameter cubic equation is in the following form:

\[ Z_n = \frac{P V}{RT} - \frac{(\sum_i \sum_j a_{ij})/RT}{v - \ell_m - \frac{T^{1/2}(v + \sum_i \ell_i)}{\ell_m}} \]

where

\[ \ell_m = (1/4)(3 \sum_i \sum_j x_i x_j \ell_{ij} + \sum_i x_i \ell_{ii}) \]

\[ \ell_{ij} = (\ell_{ii}^{1/3} + \ell_{jj}^{1/3})^{3/8} \]

\[ a_{ii} = 0.48748 \frac{R^2 T_{ci}}{P_{ci}} \]

and \[ \ell_{ii} = 0.064662 \frac{R T_{ci}}{P_{ci}} \]

It is shown that this equation of state is more accurate than the Redlich-Kwong equation, which has been considered to be the best two-constant-parameter cubic equation of state. This new equation is applied for calculation of thermodynamic properties of hydrocarbons and other non-associating fluids and fluid mixtures of interest in the oil and gas industries.

INTRODUCTION

The success of oil and gas recovery, production, and processing operations is related to the availability of accurate and simple equations of state for prediction of thermodynamic properties of fluids. Recent developments in modeling the phase behavior of reservoir fluids indicate that more serious considerations must be given to fundamental approaches to produce simple and accurate equations of state\(^1-9\). Although, there has been considerable progress made in the development of equations of state based on the statistical mechanics, the cubic equations of state are still widely preferred in industrial calculations. Equations such as the van der Waals, Redlich-Kwong, Heyen and their modifications are extensively used in petroleum and natural gas engineering calculations\(^1-7\).

In this report, we first present a simplified, but accurate, equation for the positive (repulsive) term of equations of state. Then we introduce a new version of cubic equations of state using the simplified repulsive term developed in part 1. A new cubic equation of state which contains two constant parameters is then introduced. The resulting equation of state is used for property prediction of a variety of hydrocarbons, other fluids, and mixtures of practical interest. This equation of state is shown to be a simple cubic equation with superior accuracy than the RK equation which has been considered to be the most accurate two-constant-parameter cubic equations of state.

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THE NEW REPULSIVE TERM OF EQUATIONS OF STATE

The importance of short-range repulsive forces in an equation of state for determining the thermodynamic properties of fluids is well established by the works of numerous investigators. This is because more accurate expression for the repulsive term of an equation of state results in a better agreement with the experimental data. However, the major weakness of the industrial equations of state is due to their inaccurate repulsive term.

An accurate equation for representing the repulsive effect is the MCSL equation which reduces to the following form for pure fluids:

\[ Z_{\text{rep}} = \frac{Pv}{RT} = \frac{v}{v - b}. \]  

This equation can replace the repulsive term \( v/(v-b) \) in the cubic equations. However, due to the fact that after this modification the resulting equation of state was not going to be cubic any more Scott introduced the following equation for the repulsive term of pure fluid equations of state:

\[ Z_{\text{rep}} = \frac{Pv}{RT} = \frac{(v + 0.5b)}{(v - 0.5b)}. \]  

Similarly, Kim, et al. (1986) presented another equation for repulsive term of equations of state:

\[ Z_{\text{rep}} = \frac{Pv}{RT} = \frac{(v + 0.77b)}{(v - 0.42b)}. \]

Neither of the above two equations are accurate enough to replace eq.(2) as it is demonstrated in Figure 1. In order to produce a simple, but accurate, repulsive term for cubic equations of state, we consider a number of representative cubic equations of state in a generalized from as shown in Table 1.

Table 1: Parameters of a generalized equation of state

<table>
<thead>
<tr>
<th>Equation of State</th>
<th>( E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Van der Waals</td>
<td>0</td>
</tr>
<tr>
<td>Heyen</td>
<td>0</td>
</tr>
<tr>
<td>Peng-Robinson</td>
<td>0</td>
</tr>
<tr>
<td>Redlich-Kwong</td>
<td>1/2</td>
</tr>
</tbody>
</table>

\( v_{\text{min}} \) appearing in Table 1 is the smallest molar volume for fluids which can be calculated based on different equations of state (approximately the molar volume at the triple-point) when the MCSL repulsive equation of state is used to modify the above equations (replacing \( v/(v-b) \) with eq. 2). Of course the MCSL equation of state is valid for \( v/b \) values as low as 0.25. Considering the fact that the \( v/b \) in the cubic equations of state (excluding the van der Waals equation which, because of its inaccuracy, is not used for practical calculations) do not go below 0.7 we propose the following repulsive equation of state for \( v/b > 0.7 \):

\[ Z_{\text{rep}} = \frac{Pv}{RT} = \frac{(v + 0.62b)}{(v - 0.47b)}. \]

This equation reproduces the MCSL equation for the repulsive fluid with good accuracy for \( v/b > 0.7 \) as it is demonstrated in Figures 1 and 2. In Figure 1 the percentage deviation of calculating the repulsive compressibility factor from the exact MCSL equation as calculated by eq. (5) is compared with the Scott and Kim, et.al models. According to this figure eq. (5) is in better agreement with the MCSL equation than the other simplified repulsive equations for \( v/b > 0.7 \).

In Figure 2 the repulsive excess Helmholtz free energy (over the ideal gas),

\[ (A - A_{\text{mg}})/RT = -2.319 \ln(1 - 0.47b/v) \]

as derived from eq. (5) is compared with the similar calculations using the Scott and Kim, et.al models. According to this figure eq. (6) is in better agreement with the accurate MCSL equation of state than the other simplified repulsive models.

We have extended the applicability of equations (5) and (6) to repulsive mixtures by writing them in the following forms

\[ Z_{\text{m(rep)}} = \frac{(v + 0.62b_m)}{(v - 0.47b_m)} \]

and using the following mixing and combining rules,

\[ b_m = (1/4) \sum x_i b_i \]

where;

\[ b_y = (b_y^{1/3} + b_y^{1/3})^3 / 8 \]

Eqs. (7) and (8), joined with eq. (9), are tested extensively for discrete as well as polydisperse repulsive mixtures and it is shown to be in very good agreement with the
accurate, but complicated, MCSL\textsuperscript{11} repulsive mixture equation for \(v/b > 0.7\). We have calculated the thermodynamic properties of equimolar binary mixtures \((x_1=x_2=1/2)\) with \((b_{22}/b_{11})^{1/3} = 1.5, 2.0, 2.5, \) and 3.0. The results of these calculations are compared with the accurate MCSL repulsive mixture equation of state as reported in Figures 3 and 4. The maximum percentage deviation of the binary repulsive mixture compressibility factor and excess Helmholtz free energy for molecular diameter ratios of \((b_{22}/b_{11})^{1/3} = 1.5 \) to 3 is calculated to be 3\% for \(v/b > 0.7\), which is in the range of accuracy of MCSL equation.

In order to test further the accuracy of the proposed repulsive term of the mixture equation for multicomponent mixtures we have used it to calculate thermodynamic properties of polydisperse (continuous) repulsive systems through different distribution functions \(f(r)\). Following the method of Salacuse and Stell\textsuperscript{16} we can express eq.(9) for the polydisperse systems as the following:

\[
b_m = (1/16) (7m_3 + 9m_1 m_2) \tag{10}
\]

Where, \(m_1, m_2, m_3\) are the first, second and third moments of distribution function, respectively, defined as:

\[
m_1 = \int_0^\infty r f(r) \, dr \tag{11}
\]

For the normal distribution:

\[
f_N(r) = (1/2\pi \eta)^{1/2} \exp[-(r - \bar{r})^2/2\eta] \tag{12}
\]

the moments are given by:

\[
m_1 = \bar{r} + (2\eta/\pi)^{1/2} \tag{13}
\]

\[
m_2 = \bar{r}^2 + \eta + 2(2\eta/\pi)^{1/2} \tag{14}
\]

\[
m_3 = \bar{r}^3 + 2(2\eta/\pi)^{3/2} \bar{r} + 3\eta \bar{r} + 3 \bar{r}^2(2\eta/\pi)^{1/2} \tag{15}
\]

where \(\eta\) and \(\bar{r}\) are the variance and mean, respectively. Therefore, the mixture \(b_m/v\), eq. (10) for the normal distribution is as the following:

\[
b_m/v = 4(2\pi \eta)^{1/2} \left[ 1 + (2\eta/\pi) + (1.875\pi + 2.25)\eta + (1.4375\pi)\eta^{1/2} \right] \tag{16}
\]

We can calculate the compressibility factor and Helmholtz free energy of this polydisperse repulsive mixture by joining eq. (16) with eq's (7) and (8).

For the Schultz distribution:

\[
f_s(r) = \frac{1}{s!} \left( \frac{\eta}{\bar{r}} \right)^{s+1} \bar{r}^s \exp\left[-(s+1)\eta r \bar{r} \right] \tag{17}
\]

where \(\Gamma\) is the first moment of the distribution, and \(s\) is related to variance of \(f_s(r)\) by,

\[
\eta(r) = \text{var}(r) = \frac{\bar{r}^2}{s+1} \tag{18}
\]

we can derive the following expressions for the \(b_m/v\) of the Schultz polydisperse repulsive mixture:

\[
b_m/v = 4 \left( \frac{2\pi \eta}{\bar{r}} \right)^{1/2} \left( \frac{s+2}{8(s+1)^{3/2}} \right) \tag{19}
\]

Then by replacing this equation in eq's (7) and (8) we can calculate the compressibility factor and Helmholtz free energy of the Schultz polydisperse repulsive fluids.

We have calculated the thermodynamic properties of polydisperse repulsive mixtures obeying the normal and schultz distributions. The results of these calculations are compared with the accurate polydisperse MCSL repulsive equation of state\textsuperscript{11} in Figures 5 to 8. According to these figures the deviations of the multi-component repulsive mixture compressibility factor and Helmholtz free energy for Schultz (with \(\Gamma=1\) & \(\eta=1/3,1/6,1/11\)) and normal (with \(\Gamma=1\) & \(\eta=0.1,0.3,0.5\)) distributions are quite low and acceptable for \(v/b > 0.7\) range of interest in industrial equations of state.

We have also made calculations for values of \(\bar{r}\) other than unity with similar results as to Figures 5-8 which are not be reported here due to space limitation.

At this stage we propose the following modified equation of state:

\[
Z = P/v/RT = (v+0.62b)/(v+0.47b)-(av/RT)/T \left[ 1 - \frac{\eta}{v^2} + \mu(v-\rho)bc \right] \tag{20}
\]

The difference between this equation and the generalized equation reported in Table 1 is the replacement of the new repulsive compressibility factor given by eq (5). Provided the proper numerical values of \(E_r, \mu, \eta, \) and \(bc\) are replaced in this equation one can reproduce the new versions of the equations of state.
reported in Table 1. It should be pointed out that this change of the repulsive term will not keep the Peng-Robinson and Heyen equations in cubic forms any more.

By applying the critical point constraints: 
\[ \left( \frac{\partial P}{\partial v} \right)_{T_c} = \left( \frac{\partial^2 P}{\partial v^2} \right)_{T_c} = 0 \] 
(for all equations) and 
\[ Z = Z_c \] 
(for the three-parameter equations like Heyen) we can derive expressions for parameters of the new version of equations of state with respect to the critical properties as reported in Table 2.

Table 2: Parameters of eq. (20) with respect to the critical properties.

<table>
<thead>
<tr>
<th>Equation of State</th>
<th>( a/RT )</th>
<th>( b/v_c )</th>
<th>( c/v_c )</th>
<th>New</th>
<th>Original</th>
</tr>
</thead>
<tbody>
<tr>
<td>Van der Waals</td>
<td>1.429</td>
<td>0.542</td>
<td>0.364</td>
<td>0.375</td>
<td></td>
</tr>
<tr>
<td>Heyen</td>
<td>1.945</td>
<td>0.371</td>
<td>0.997</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>Peng-Robinson</td>
<td>1.951</td>
<td>0.370</td>
<td>0.272</td>
<td>0.327</td>
<td></td>
</tr>
<tr>
<td>Redlich-Kwong</td>
<td>1.513</td>
<td>0.341</td>
<td>0.314</td>
<td>0.333</td>
<td></td>
</tr>
</tbody>
</table>

*These values are based on \( Z_c = 0.27 \).

According to this table, except for the Heyen equation for which \( Z_c \) is an input parameter, the \( Z_c \) values calculated based on the new version of the other equations of state are closer to the experimental \( Z_c \) values than the \( Z_c \)'s calculated by the original form of the equations of state.

THE NEW TWO-CONSTANT-PARAMETER CUBIC EQUATION OF STATE

By replacing \( \epsilon_l = 0 \) in eq. (20) it will become a cubic equation in the following form:
\[ Z = (v + 0.62b)/(v - 0.47b) - (a/RT)/T^\epsilon (v + \beta). \] (21)

The choices of \( \epsilon \) and \( \beta \) are still in our disposal. For the sake of simplicity we choose \( \epsilon = 1/2 \), as proposed by Redlich and Kwong, and \( \beta = 0.47b \) as appears in the denominator of the repulsive term of eq. (21). As a result we introduce a new cubic equation of state in the following form:
\[ Z = (v + 1.13191)/(v - \beta) - (a/RT)/T^{1/2}(v + \beta). \] (22)

Equation (22) is a cubic equation of state in terms of volume and contains only two constant parameters. By applying the critical point constrains, we determine parameters \( a \) and \( \beta \) as the following:
\[ a = 0.48748 \frac{R T_c^2}{P_c^{5/2}} \] and \[ \beta = 0.064662 \frac{R T_c}{P_c} \] (23)

The critical compressibility factor \( Z_c = 0.333 \) will remain the same as the RK equation of state. In order to demonstrate the validity of the repulsive term of this equation of state we have calculated \( \nu_{min}/b \) as reported in Table 3 for different fluids. According to this table for all the fluids studied \( \nu_{min}/b \) values are in the allowable range of \( \nu/b > 0.7 \) where the repulsive part of eq.(22) accurately represents the MCSL repulsive equation of state.

Table 3: Calculation of the minimum \( \nu/b \) ratio for different fluids according to Eq. (23).

<table>
<thead>
<tr>
<th>Fluid</th>
<th>( \nu_{min}/b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>0.76</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.76</td>
</tr>
<tr>
<td>n-Propane</td>
<td>0.73</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.80</td>
</tr>
<tr>
<td>Isobutane</td>
<td>0.73</td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.80</td>
</tr>
<tr>
<td>N(_2)O(_4)</td>
<td>0.89</td>
</tr>
<tr>
<td>H(_2)S</td>
<td>0.86</td>
</tr>
<tr>
<td>NF(_3)</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Extension of equation (22) to mixtures will take the following form:
\[ Z = \frac{P v}{RT} = \frac{v + 1.3191 \nu_m}{v - \nu_m} - \left( \frac{\sum_i \sum_j a_{ij}}{RT} \right) \] (24)

where \( \nu_m = \frac{1}{4} \sum_i \sum_j x_i x_j \nu_{ij} + \sum_i \nu_i \) and \( \nu_{ij} = \left( \nu_{i}^{1/3} + \nu_{j}^{1/3} \right)^{3/2} \) and \( a_{ij} = (1 - k_{ij})^{a_{ij}} a_{ij}^{1/2} \).

In eq. (24) we have applied the new mixing rule for repulsive term (eq. 9). For the attractive term, we have used the usual cubic equation mixing rules in order to be able to observe the corrections in the repulsive term of this equation for mixture calculations. It should be pointed out that there are also other possibilities for the mixing rules of the attractive term of this equation of state[15]. This new equation of state is used to predict properties of pure fluids and mixtures as it is reported below.
RESULTS AND DISCUSSION

Cubic equations of state may be classified into two categories: (i) Those with two constant parameters like the van der Waals, Berthelot, Dieterici, and Redlich-Kwong (RK) equations. (ii) Those with more than two parameters (or two or more temperature-dependent parameters) and they include the Peng-Robinson, Heyen and Soave equations. Among the first category of cubic equations of state the RK equation is still considered to be the most accurate equation of all. As a result in order to test the accuracy of eq. (22), which is also of the first category of equations, for prediction of the properties of pure fluids and mixtures it is compared here with the RK equation. Table 4 shows the comparisons of the result of density calculations using eq. (22) with the RK equation and the experimental data. According to this table the result of eq. (22) are generally superior to the RK equation for 17 out of 19 pure fluids tested.

In order to test the applicability of eq. (24) for mixtures, we have used it for calculation of the properties of a number of systems. In all the calculations reported here for eq. (24), and for the RK equation, we have chosen the value of the unlike-interaction parameters, $k_{ij}$'s, equal to zero. This choice of $k_{ij}=0$ is made in order not to complicate the comparisons of different equations of state with the fitting of their $k_{ij}$'s. However, for more accurate calculations of mixture properties this parameter may be fitted to some mixture data.

On Figures 9 and 10 the density calculations for two different binary high-pressure (500 bar) liquid mixtures (n-octane + n-dodecane and n-decane + n-tetradecane) are reported and are compared with the results of the RK equation. According to these figures predictions by eq. (24) are better than the RK equation.

We also have performed solubility and VLE calculations for mixtures. On Figure 11 the solubility of methane in n-hexane is reported versus temperature at two different pressures of 40.5 and 81.1 bars. According to this figure also the predictions by eq. (24) are closer to the experimental data than the RK equation.

In Figures 12 to 14 equilibrium pressure-composition diagrams for methane + n-decane (at 344.26 K), carbon dioxide + n-decane (at 344.26 K), and for nitrogen + carbon dioxide system (at $T = 270.0$ K) are reported. According to these three figures the predictions by eq. (24) are far better than the predictions by the RK equation.

As it was mentioned earlier, in all the calculations reported here, the unlike interaction parameters, $k_{ij}$'s, are assumed to be zero. By choosing appropriate non-zero $k_{ij}$ values the proposed equation of state would accurately correlate and predict properties of the mixtures reported in this paper. The $k_{ij}$ data bank for this equation is not reported here due to space limitation.

The proposed equation of state may be made even more accurate by choosing its parameters ($a$ & $b$) to be dependent on temperature as it is usually done in other industrial equations of state.

ACKNOWLEDGEMENTS

This research is supported in part by the National Science Foundation, Grant No. CTS-9108595.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$A$</td>
<td>Helmholtz free energy</td>
</tr>
<tr>
<td>$a$</td>
<td>attractive constant in equation of state</td>
</tr>
<tr>
<td>$b$</td>
<td>repulsive constant in equation of state</td>
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<tr>
<td>$c$</td>
<td>third parameter in equations of state</td>
</tr>
<tr>
<td>$f_{ij}(R)$</td>
<td>distribution function</td>
</tr>
<tr>
<td>$K_{ij}$</td>
<td>binary interaction parameter</td>
</tr>
<tr>
<td>$N_0$</td>
<td>Avogadro number</td>
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<tr>
<td>$P$</td>
<td>pressure</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
</tr>
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<td>$r$</td>
<td>random variable</td>
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<tr>
<td>$T$</td>
<td>absolute temperature</td>
</tr>
<tr>
<td>$x$</td>
<td>mole fraction</td>
</tr>
<tr>
<td>$Z$</td>
<td>compressibility factor</td>
</tr>
<tr>
<td>$s$</td>
<td>a parameter in Schultz distribution function, defined in eq.(19)</td>
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Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>density</td>
</tr>
<tr>
<td>$\pi$</td>
<td>$3.1415927$</td>
</tr>
<tr>
<td>$\eta$</td>
<td>variance of normal distribution function</td>
</tr>
</tbody>
</table>

Subscripts

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$</td>
<td>critical property</td>
</tr>
<tr>
<td>$i,j$</td>
<td>component indices</td>
</tr>
<tr>
<td>$i,j$</td>
<td>property of $i,j$ interaction</td>
</tr>
<tr>
<td>$i,g$</td>
<td>ideal gas property</td>
</tr>
<tr>
<td>$m$</td>
<td>mixture property</td>
</tr>
<tr>
<td>$N$</td>
<td>normal distribution</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Schultz distribution</td>
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</tbody>
</table>

As it was mentioned earlier, in all the calculations reported here, the unlike interaction parameters, $k_{ij}$'s, are assumed to be zero. By choosing appropriate non-zero $k_{ij}$ values the proposed equation of state would accurately correlate and predict properties of the mixtures reported in this paper. The $k_{ij}$ data bank for this equation is not reported here due to space limitation.

The proposed equation of state may be made even more accurate by choosing its parameters ($a$ & $b$) to be dependent on temperature as it is usually done in other industrial equations of state.

ACKNOWLEDGEMENTS

This research is supported in part by the National Science Foundation, Grant No. CTS-9108595.
REFERENCES


Table 4: Comparison of this work and RR equations of state for density prediction of different compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature Range (K)</th>
<th>Pressure Range (atm)</th>
<th>No. of Data</th>
<th>RR</th>
<th>THIS WORK</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>250-1000</td>
<td>40-400</td>
<td>143</td>
<td>3.9</td>
<td>2.4</td>
</tr>
<tr>
<td>H₂</td>
<td>300-700</td>
<td>9-400</td>
<td>101</td>
<td>1.8</td>
<td>2.2</td>
</tr>
<tr>
<td>O₂</td>
<td>300-1000</td>
<td>10-700</td>
<td>133</td>
<td>4.0</td>
<td>2.4</td>
</tr>
<tr>
<td>N₂</td>
<td>200-1000</td>
<td>8-500</td>
<td>120</td>
<td>1.9</td>
<td>2.7</td>
</tr>
<tr>
<td>Methane</td>
<td>91-500</td>
<td>10-700</td>
<td>170</td>
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<td>3.4</td>
</tr>
<tr>
<td>Propane</td>
<td>200-700</td>
<td>5-700</td>
<td>140</td>
<td>3.1</td>
<td>3.6</td>
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<tr>
<td>i-Butane</td>
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<td>3.1</td>
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<td>n-Pentane</td>
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<td>5-400</td>
<td>60</td>
<td>3.1</td>
<td>2.9</td>
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<td>n-Hexane</td>
<td>260-1000</td>
<td>1-500</td>
<td>100</td>
<td>5.7</td>
<td>3.3</td>
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<td>n-Heptane</td>
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<td>1-500</td>
<td>100</td>
<td>5.8</td>
<td>2.8</td>
</tr>
<tr>
<td>n-Octane</td>
<td>320-1000</td>
<td>1-500</td>
<td>80</td>
<td>6.3</td>
<td>2.2</td>
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<tr>
<td>n-Nonane</td>
<td>300-600</td>
<td>15-1000</td>
<td>90</td>
<td>7.9</td>
<td>2.6</td>
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<tr>
<td>n-Decane</td>
<td>300-500</td>
<td>15-500</td>
<td>130</td>
<td>8.8</td>
<td>2.5</td>
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<td>n-Dodecane</td>
<td>300-570</td>
<td>1-500</td>
<td>20</td>
<td>11.3</td>
<td>3.7</td>
</tr>
<tr>
<td>n-Tridecane</td>
<td>300-600</td>
<td>90-1050</td>
<td>50</td>
<td>13.2</td>
<td>4.7</td>
</tr>
<tr>
<td>n-tetradecane</td>
<td>300-600</td>
<td>1-600</td>
<td>30</td>
<td>15.6</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Overall: 1992 6.2 3.1

Figure 1 - The percentage deviation of compressibility factor from the exact MCSL hard-sphere equation of state versus the reduced density, b_2/(8v_b), for the pure hard sphere fluid.

Figure 2 - The excess Helmholtz free energy according to different approximations and the exact MCSL hard-sphere equation of state versus the reduced density, b_2/(8v_b), for the pure hard sphere fluid.

Figure 3 - The percentage deviation of compressibility factor from the exact mixture MCSL hard-sphere equation versus the mixture reduced density, (b_2/v_b)_(mix), and for different molecular diameter ratios for binary mixtures of hard-sphere fluids.

Figure 4 - The excess Helmholtz free energy according to Eq. (2) and the exact MCSL hard-sphere mixture equation of state versus the reduced density, (b_2/v_b)_(mix), for the binary mixture hard-sphere fluid with (b_2/v_b)_(mix) = 3. For (b_2/v_b)_(mix) ratios less than 3 the two theories would match even better than this reported case.

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Figure 8 - The relative deviation of compressibility factor from the exact mixture MSSL hard sphere equation of state for the polydisperse hard sphere mixture with normal distribution, versus the mixture reduced density, $\beta \frac{\bar{N}_p \rho_m}{\bar{N}_p \rho_m^{\infty}}$, and for mean value of $\bar{r} = 1$ and different variances. The third moment $m_3$ of the normal distribution is defined by eq. (18).

Figure 6 - The excess Helmholtz free energy according to Eq. (6) and the exact MSSL hard sphere mixture equation of state versus the reduced density, $\frac{\mu \bar{N}_p \rho_m}{\bar{N}_p \rho_m^\infty}$, for the polydisperse hard sphere mixture with normal distribution with mean value of $\bar{r} = 1$ and variance $\sigma^2 = 0.1$. For variances less than 0.3 the two theories would match even better than this reported case.

Figure 9 - The calculated percentage deviation of (n-octane + n-dodecane) liquid mixture density from the experimental data [18], according to the present and RK mixture equations of state $\rho_p = 0$, versus n-dodecane mole fraction at $T = 298.15$ K and $P = 500$ bar.

Figure 10 - The calculated percentage deviation of (n-decane + n-tetradecane) liquid mixture density from the experimental data [18], according to the present and RK mixture equations of state $\rho_p = 0$, versus n-tetradecane mole fraction at $T = 298.15$ K and $P = 500$ bar.

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Figure 11 - Predictions of the solubility of methane in n-hexane according to the present and RK mixture equations of state (P,T=0) versus temperature at two different pressures. The experimental data reported on this graph are taken from Ref.[18].

Figure 12 - Prediction of the equilibrium pressure-composition diagram for (carbon dioxide + n-decane) system according to the present and RK equations of state (P,T=0), at 344.26 K. The experimental data reported on this graph are taken from Ref.[20].

Figure 13 - Prediction of the equilibrium pressure-composition diagram for (methane + n-decane) system according to the present and RK equations of state (P,T=0), at 344.26 K. The experimental data reported on this graph are taken from Ref.[21].

Figure 14 - Prediction of the equilibrium pressure-composition diagram for (dihydrogen + carbon dioxide) system according to the present and RK equations of state (P,T=0), at 270 K. The experimental data reported on this graph are taken from Ref.[22].