Impact of Equation of State on Simulating CO$_2$ Pipeline Decompression

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CO$_2$ Properties and EoS for Pipeline Engineering
11 August 2013, Athens, Greece
1. Background

2. Equations of State

3. Impact on simulation of pipeline decompression

4. Conclusions
1. Background
A ductile fracture will come to rest when the fluid pressure at the crack tip, $P_t$, falls below the Crack Arrest Pressure, $P_a$. Running fractures represent a threat to CO$_2$ pipelines.
Pipeline decompression

- At the rupture plane the fluid is exposed to ambient air
- Following the rupture, the rarefaction wave starts propagating along the pipe at the speed of sound
- The vapour phase emerges in the expansion wave reducing the mixture speed of sound
- Due to rapid cooling of the fluid in the decompression wave, the solid phase may also be released from the pipe
1. Background

2. Equations of State
Cubic Equations of State

Generalized cubic EoS

\[ z^3 - (1 - B^* - uB^*)z^2 + (A^* + \omega B^{*2} - uB^* - uB^{*2})z - A^*B^* - \omega B^{*2} - \omega B^{*3} = 0 \]

\[ A^* = \frac{aP}{RT^2}, \quad B^* = \frac{bP}{RT} \]

<table>
<thead>
<tr>
<th>EoS</th>
<th>(a)</th>
<th>(b)</th>
<th>(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RK</td>
<td>0.42748 ( \frac{R^2(T_c)^{2.5}}{P_c} )</td>
<td>0.08664 ( \frac{RT_c}{P_c} )</td>
<td>0.08664 ( \frac{RT_c}{P_c} )</td>
</tr>
<tr>
<td>u=1, w=0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SRK</td>
<td>0.42748 ( \frac{R^2(T_c)^{2.5}}{P_c} )</td>
<td>0.08664 ( \frac{RT_c}{P_c} )</td>
<td>0.08664 ( \frac{RT_c}{P_c} )</td>
</tr>
<tr>
<td>u=1, w=0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PR</td>
<td>0.45724 ( \frac{R^2(T_c)^{2}}{P_c} )</td>
<td>0.07780 ( \frac{RT_c}{P_c} )</td>
<td>0.07780 ( \frac{RT_c}{P_c} )</td>
</tr>
<tr>
<td>u=2, w=-1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PR/G</td>
<td>0.45724 ( \frac{R^2(T_c)^{2}}{P_c} )</td>
<td>0.07780 ( \frac{RT_c}{P_c} )</td>
<td>0.07780 ( \frac{RT_c}{P_c} )</td>
</tr>
<tr>
<td>u=2, w=-1</td>
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</tbody>
</table>

\[ a(T) = [1 + \alpha(T)] \]

\[ \alpha(T) = \frac{R^2(T_c)^{2.5}}{P_c} \]
The SAFT (Statistical Associating Fluid Theory) equation of state is written as a summation of residual Helmholtz free energy terms that occur due to different types of molecular interactions in the system under study.

Hard sphere term:
\[
\frac{A_{\text{hs}}}{RT} = \frac{4n - 3n^2}{(1 - n)^2}
\]
Carnahan-Starling EoS for hard spheres

Chain term:
\[
\frac{A_{\text{chain}}}{RT} = (1 - m) \ln \left( \frac{1 - 0.5n}{(1-n)^3} \right)
\]
based on Wertheim’s TPT1

Association term:
\[
\frac{A_{\text{assoc}}}{RT} = \sum_{A=1}^{M} \left( \ln X^A - \frac{X^A}{2} \right) + \frac{1}{2}M
\]
based on TPT1

Dispersion term:
\[
\frac{A_{\text{disp}}}{RT} = \sum_{i=1}^{4} \sum_{j=1}^{9} D_{ij} \left( \frac{u}{kT} \right)^i \left( \frac{n}{\tau} \right)^j
\]
Alder equation from molecular dynamics
1. Background

2. Equations of State

3. Impact on simulation of pipeline decompression
Saturated density predictions

Saturated liquid and vapour density predictions using the various Equations of State
### Accuracy of derivative properties

<table>
<thead>
<tr>
<th></th>
<th>SAFT</th>
<th>PC-SAFT</th>
<th>RK</th>
<th>PR</th>
<th>SRK</th>
<th>Yokozeki</th>
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</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.81</td>
<td>1.14</td>
<td>6.25</td>
<td>4.89</td>
<td>5.97</td>
<td>3.35</td>
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<tr>
<td>Cv</td>
<td>6.37</td>
<td>3.77</td>
<td>9.96</td>
<td>3.94</td>
<td>8.80</td>
<td>58.75</td>
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<tr>
<td>Cp</td>
<td>11.09</td>
<td>3.53</td>
<td>10.35</td>
<td>4.54</td>
<td>3.35</td>
<td>28.76</td>
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<tr>
<td>Sound Speed</td>
<td>6.73</td>
<td>3.26</td>
<td>16.65</td>
<td>13.53</td>
<td>11.86</td>
<td>15.39</td>
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<tr>
<td>Joule-Thomson</td>
<td>113.11</td>
<td>44.20</td>
<td>75.70</td>
<td>102.08</td>
<td>66.65</td>
<td>85.62</td>
</tr>
</tbody>
</table>

Comparison of the predictive accuracy of EoS (AAD%) for important derivative properties.
Speed of Sound predictions

Saturated vapour phase speed of sound

Saturated liquid phase speed of sound
Vapour phase decompression

Pressure history during decompression

13.5 m from open end

Pressure history during decompression
18 m from open end
Liquid phase decompression

Pressure history during decompression 143 m from open end
1. Background

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4. Conclusions
• Accuracy of speed of sound in liquid predicted by even complex EoS remarkably low

• This greatly affects the modelling of the decompression wave, given that its front moves at the speed of sound

• Very little experimental data for dense phase speed of sound available for development of better EoS

• Results presented relate to pure CO$_2$ only, the little impure CO$_2$ data we have indicates that the same observations are true
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