

Section 2.5

Multi-parameter Equations of State

The last class of equations of state we will discuss are multi-parameter equations of state. The objective of the previous equations of state was to model a large range of species with (preferably) as few parameters as possible. Multi-parameter equations of state do the exact opposite: only intended to be used for a single system where you can use as many parameters as you want. The benefit of this is that these equations are *very* accurate, often considered as good as experimental data (in fact, the results one gets from NIST's chemistry webbook are typically obtained from such equations). While this does limit the equations to just one system, one often finds, in industry, most systems of interest are made up of the same species. As such, it is often worthwhile to use these equations of state with the benefit of significantly greater accuracy, in contrast to any other available.

The only 'weakness' to these equations of state is that they are intended for interpolation, not extrapolation. Typically, they will have been fitted to quite a large range of conditions, thus making it difficult to find conditions where they begin to perform badly. However, it is something to bear in mind when using these equations.

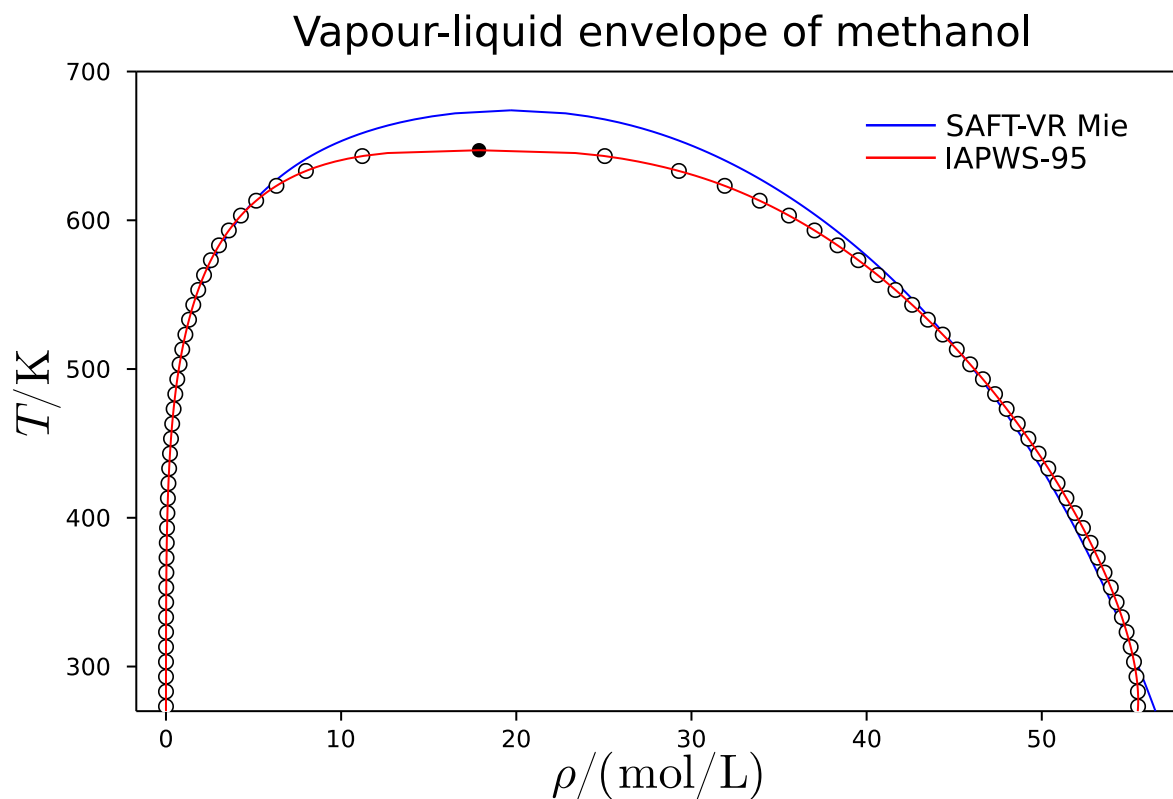
Since these equations are devoid of any actual physical intuition, we will only give two examples to illustrate their impressive accuracy, but also highlight some of their limitations.

Section 2.5.1

The International Association for the Properties of Water and Steam Equation (IAPWS-95)

This equation of state is designed for just one species: water. Despite all the improvements made with equations like SAFT, there are still significant issues that are left to be addressed. For example, even in the saturation envelope:

```
• mw = IAPWS95();
```



As we can see above, despite its advancements, SAFT-VR Mie still overestimates the critical point. Furthermore, if one looks at the saturated liquid densities around 300 K, one can see that SAFT-VR Mie is unable to predict a maxima in the liquid density. This is something that has been of interest to developers of SAFT equations for years. However, for the highly-regressed IAPWS-95 equation of state, it captures this behaviour very well.

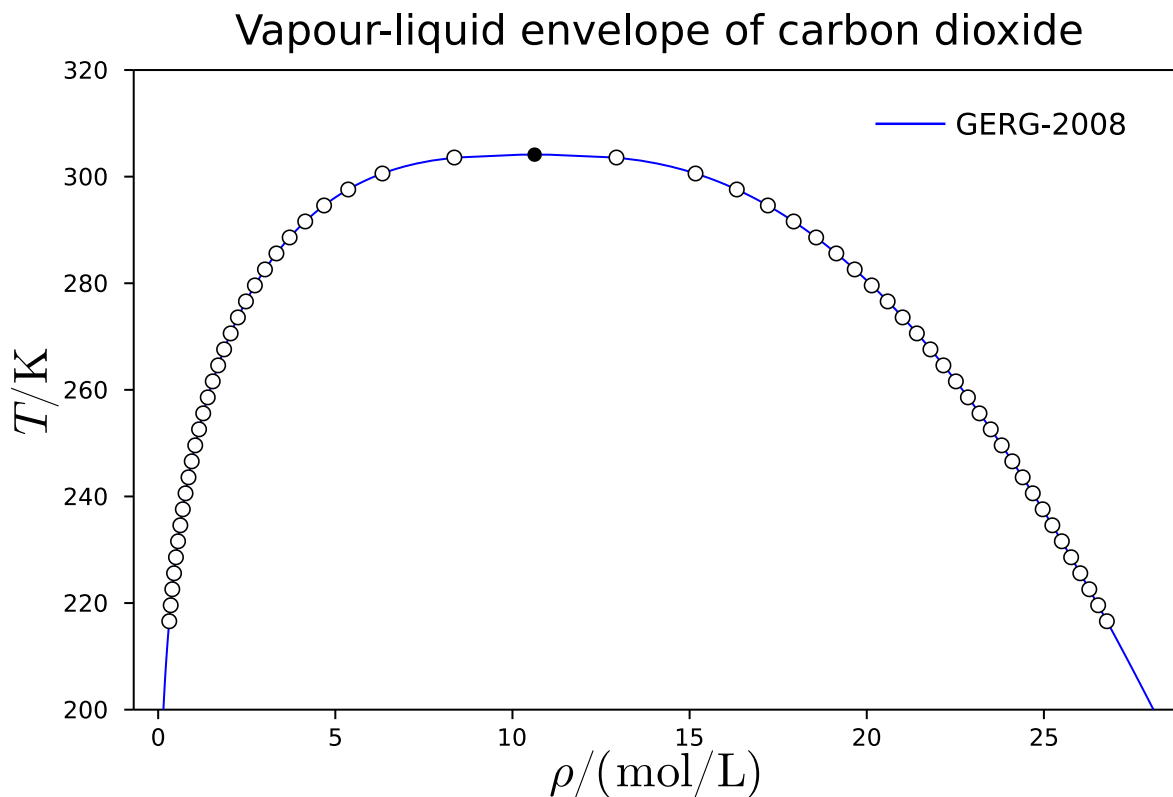
The IAPWS-95 equation was fitted using almost all data available for water, covering temperatures from 251.2 K to 1273 K, and pressures up to 1000 MPa. As such, for most practical purposes, we will always be interpolating when using IAPWS-95, making it effectively impossible to find conditions where it performs badly.

Section 2.5.2

The Groupe Européen de Recherches Gazières 2008 equation of state (GERG-2008)

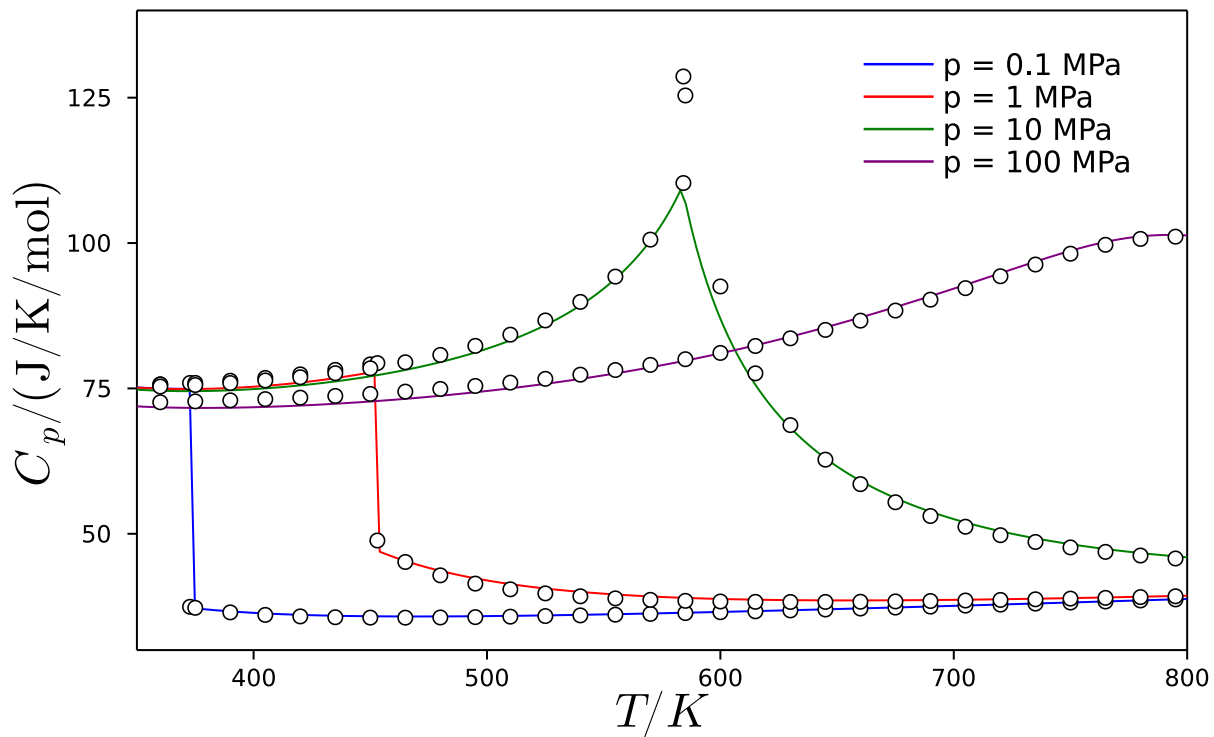
As one can imagine, a lot of experimental data has been collected for natural gas systems. As a result, this data was used to fit a high-accuracy equation of state designed solely for natural gas systems. The GERG-2008 version involves 21 different species and is able to model bulk and equilibrium properties for both pure and mixed systems very accurately:

```
• co2 = GERG2008(["carbon dioxide"]);
```



```
• h2o = GERG2008(["water"]);
```

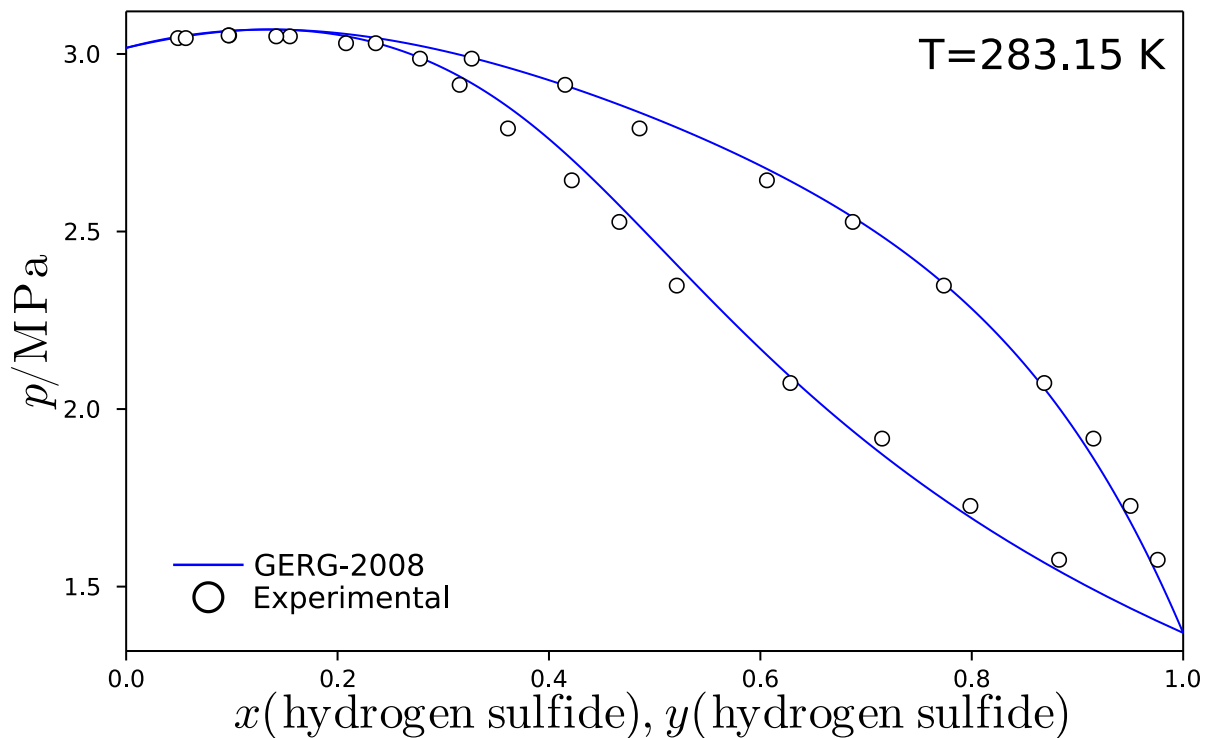
Isobaric heat capacity of water

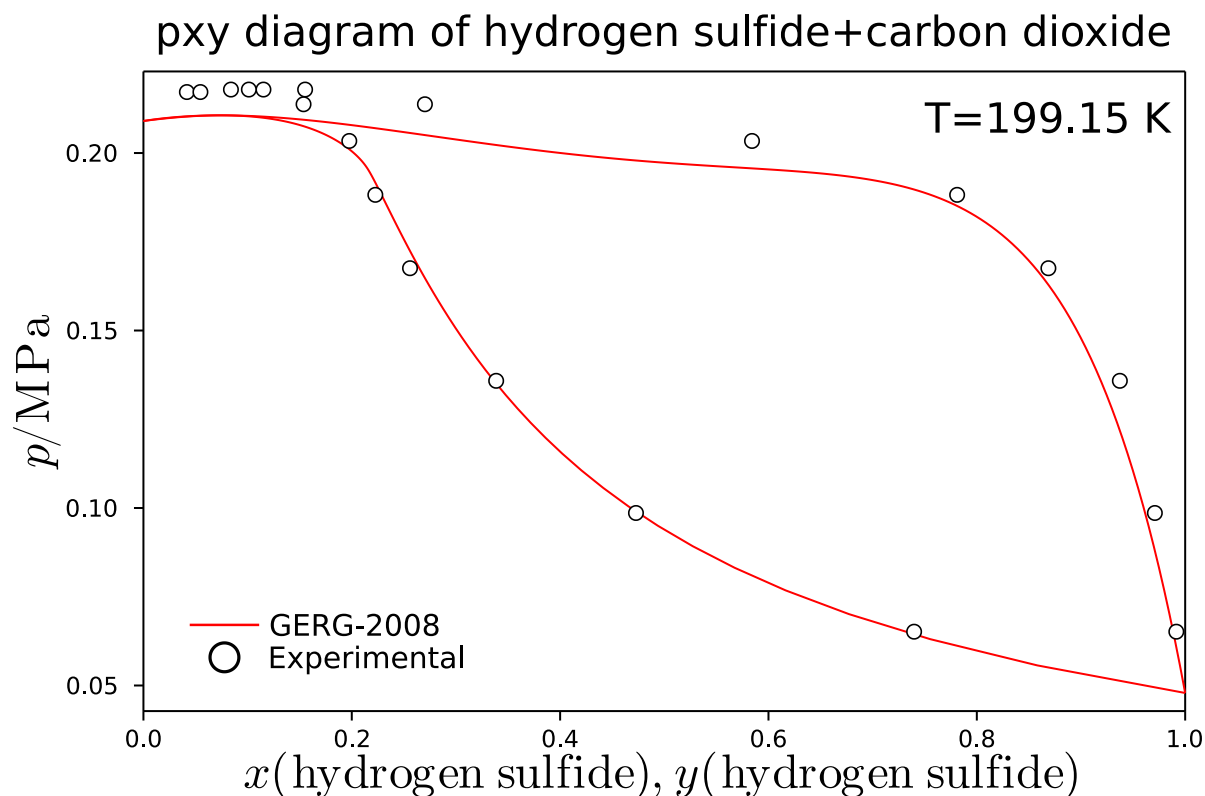


h2s_et = GERG2008 with 2 components:
 "hydrogen sulfide"
 "ethane"

```
• h2s_et = GERG2008(["hydrogen sulfide", "ethane"])
```

pxy diagram of hydrogen sulfide+carbon dioxide





The above example are intended to highlight that GERG-2008 is indeed very accurate for the conditions it was regressed in (approximately 90 to 450 K and pressures up to 35 MPa). However, when one starts to extrapolate, we can begin seeing some of the limitations of such multi-parametric equations of state. In the case of water's heat capacity, at intermediate pressures, agreement with experimental data is excellent. At much higher pressures, the model begins to struggle.

Even for binary mixtures within the temperature range it was fitted in (see hydrogen sulfide + methane phase diagrams), it begins to perform poorly. This is to be expected and serves as a reminder to always verify the results from such equations instead of using them blindly.

