Mutating Thermodynamic Properties for Use in Fitting Equations of State

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The search for bizarre thermodynamic properties for use in fitting equations of state has begun! The goal of this quest is to mutate properties in such a way that the output is no longer useful for industrial applications; rather, calculated values are only beneficial in fitting equations of state to better model the fluid's properties in regions that lack experimental data. In particular, the critical region for most substances is poorly characterized and thus "anything goes" might be the attitude of the one correlating the data to the equation. Constraints have been developed over the last few decades to alter this mindset, such as the rectilinear diameter, which allows for better modeling in the critical region, aids in the search to determine the critical density of the fluid, and, through its reflection of the liquid phase into the vapor phase, greatly decreases the uncertainty of vapor-phase properties, especially density.

Multiple properties have been mutated to aid in better performance, e.g., the isochoric heat capacity, the Gruneisen parameter, the phase identification parameter, and the effective inverse power law exponent. The simplest, the isochoric heat capacity, is simply modified by multiplying by the inverse reduced temperature taken to the fourth power. The result is a nonsensical value that has no use except in fitting; however, the benefit comes by converting a property where the signs of the slopes and third derivatives are both positive and negative as a function of temperature to something where the slope, curvature, and third and fourth derivatives are all positive. This allows the correlator to easily constrain the real isochoric heat capacity without knowing where the slopes or third derivatives change from negative to positive (which happens at different temperatures). The most complex property is the phase identification parameter, where the signs of the derivatives change multiple times above the critical point and is nearly impossible to constrain. However, through a particular mutation of multiplying by several derivatives of pressure, density, and temperature, a non-thermodynamic property has been found where the curvature of all isotherms is always positive. Constraining such a variable is quite simple, and, when done properly, always leads to nearly perfect plots of the phase identification parameter vs. density along isotherms, which is perhaps the most difficult of all plots monitored and where the outcome must be correct before an equation of state can be declared finished.