Third Generation of Fitting Constraints

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The development of modern equations of state has seen many changes brought on by the dramatic increase in the computation abilities of computers and by the combined experienced gained through a collaboration of multiple institutions world-wide. Equations of state are no longer simple fits of experimental data, but require a trained correlator who understands how the equation should behave over large ranges of temperature, pressure, and density for multiple properties, many of which have no use in practical applications, but have been proven to be more effective criteria for the quality of an equation of state. The first generation of fitting constraints involved only common properties, these generally being isochoric and isobaric heat capacities, speed of sound, and pressure-temperature-density characteristics. Constraints were often made through the use of printed diagrams, a ruler, and a pencil. Points taken from the extrapolation were then entered manually and fitted. The second generation currently in use involves software techniques to allow the fitter to use "less than" and "greater than" operators to change the shape of a property, but not fit its actual value. The properties fitted now involve the Phase Identification Parameter (PIP), the Gruneisen parameter, and the rectilinear diameter, to name a few. The third generation of fitting constraints is now in its infancy and deals with higher order derivatives of the equation of state for use in controlling the equation's behavior for fluids that have limited data but which still require a wide ranging equation for industrial applications. The characteristics of many of these higher order derivatives are still unclear, and new fits to fluids such as nitrogen, ethane, and carbon dioxide will help establish the correct behavior of each derivative.