Fitting 14-Term Equations of State with Just Two Data Points

Eric W. Lemmon [C, S]
Thermophysical Properties Division, National Institute of Standards and Technology, Boulder, CO, U.S.A.

The development of equations of state covering the liquid, vapor, and supercritical regions usually requires a substantial amount of experimental data in all regions and for a variety of properties. When data are unavailable for a particular property, correlators often resort to "graphite research" by plotting the property from an initial equation and extending it manually with a pencil and ruler. Data points are read off the paper and are then included in the fit. Such research is not always effective, and can require many iterations of fitting, plotting, and updating the data points. New fitting techniques have been developed that allow nonlinear fitters to add constraints to a fit such that the slope or curvature of an isoproperty line can be controlled, without fitting the magnitude of various properties. For example, the curvature of the heat capacities approaching the critical region can be forced to be positive along the saturation lines (liquid and vapor), thus ensuring that small bumps in the surface are not present. Furthermore, nonlinear fitting allows one to control not only the first and second derivatives, but the third and fourth ones as well to obtain a very smooth surface of state. With a significant number of constraints for the derivatives of heat capacities, speeds of sound, pressures, and so on, an equation of state can be developed that appears to be thermodynamically correct in all aspects. This approach decreases the number of data points that are required to fit an equation of state, so much in fact that an equation of state with 14 terms can be developed for a fluid with only two measurements, one for the vapor pressure and one for the saturated liquid density. This approach requires the critical point of the fluid, but that can often be estimated. The presentation will show results from such fits and describe what kind of criteria are used to control the equation.