“Fundamentals” of Equations of State

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E85 / Gasoline


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A Liquid Density Standard Over Wide Ranges of Temperature and Pressure Based on Toluene

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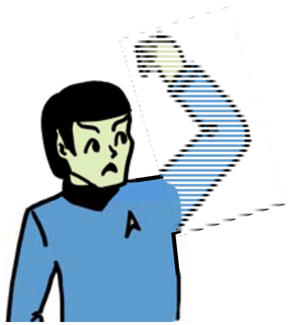
The density of liquid toluene has been measured over the temperature range −60 °C to 200 °C with pressures up to 35 MPa. A two-sinker hydrostatic-balance densimeter utilizing a magnetic suspension coupling provided an absolute determination of the density with low uncertainties.

pressure measurements. This SRM is intended for the calibration of industrial densimeters.



...a standard platinum resistance therm... ...ed with ITS–90 fixed points. The pre... ...r was calibrated against a piston gag... ...ard.

df_ρ df_V df_x df_e df_{rp}

$$df_{\mathrm{eff}} = (0.082\ \mathrm{kg/m^3})^4 \Big/ \left[\frac{(0.0086\ \mathrm{kg/m^3})^4}{886} + \frac{(0.0114\ \mathrm{kg/m^3})^4}{32} + \frac{(0.003\ \mathrm{kg/m^3})^4}{8} + \frac{(0.0292\ \mathrm{kg/m^3})^4}{9} + \frac{(0.075\ \mathrm{kg/m^3})^4}{30}\right] \quad (57)$$

$$df_{\mathrm{eff}} = 39,$$

and the appropriate coverage factor for a 95 % uncertainty interval is 2.0227.

...dix A–Experimental Values ...sity

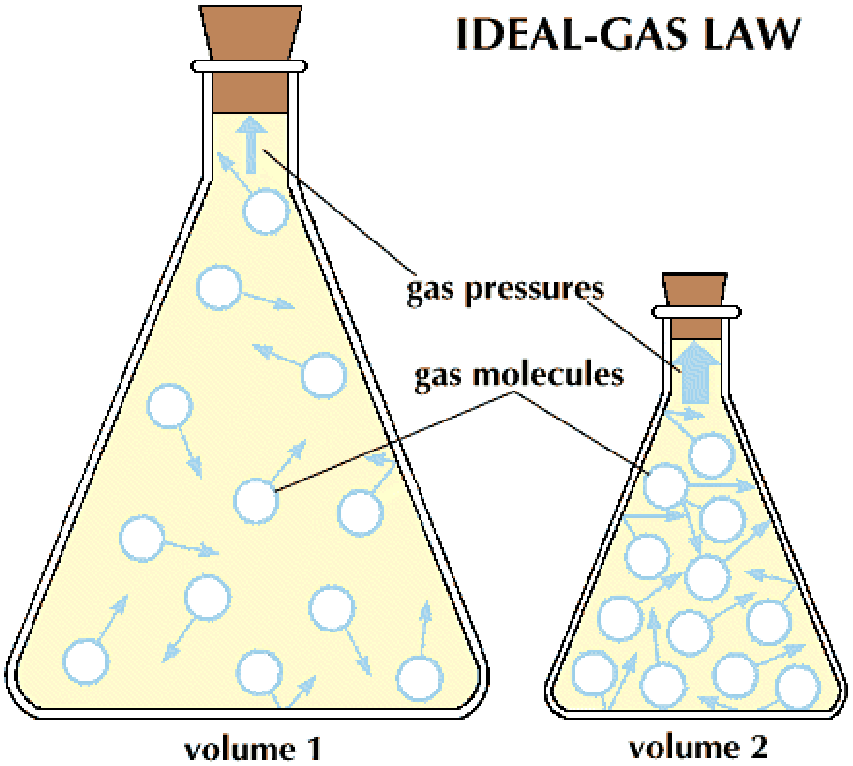
Table A1. Experimentally measured temperatures t, pressures p, a... densities ρ_{exp} for degassed SRM toluene with the standard uncertai... ty $u(\rho_{\mathrm{fluid}})$

	t (°C)	p (MPa)	ρ_{exp} (kg m^{-3})	$u(\rho_{\mathrm{fluid}})$ (kg m^{-3})
Filling 1				
	−59.999	0.0089	940.943	0.042
	−59.998	0.0090	940.942	0.042
	−59.999	0.0090	940.943	0.042
	−59.998	0.0089	940.943	0.042
	−59.998	0.0088	940.941	0.042
	−59.999	3.8239	942.780	0.042
	−59.999	3.8232	942.781	0.042
	−59.998	3.8266	942.782	0.042
	−59.999	3.8248	942.782	0.042
	−59.999	3.8249	942.781	0.042

EOS Characteristics

	Vapor Phase	Liquid Phase	Critical region	Accuracy	Speed	Iteration
Ideal gas law	√			Low	High	No
van der Waals	√	√	√	Low	High	No
Cubics	√	√	√	Moderate	High	No
Virials	√			Moderate	Med	Yes
BWRs	√	√	√	High	Med	Yes
Helmholtz	√	√	√	Very High	Low	Yes
Each calculates pressure as a function of density and temperature, except for the Helmholtz energy equation.						

$$pv = RT$$



$$\frac{pv}{RT} = 1 = Z$$

(for an ideal gas)

$$Z = 1 + B\rho$$

$$Z = 1 + B\rho + C\rho^2$$

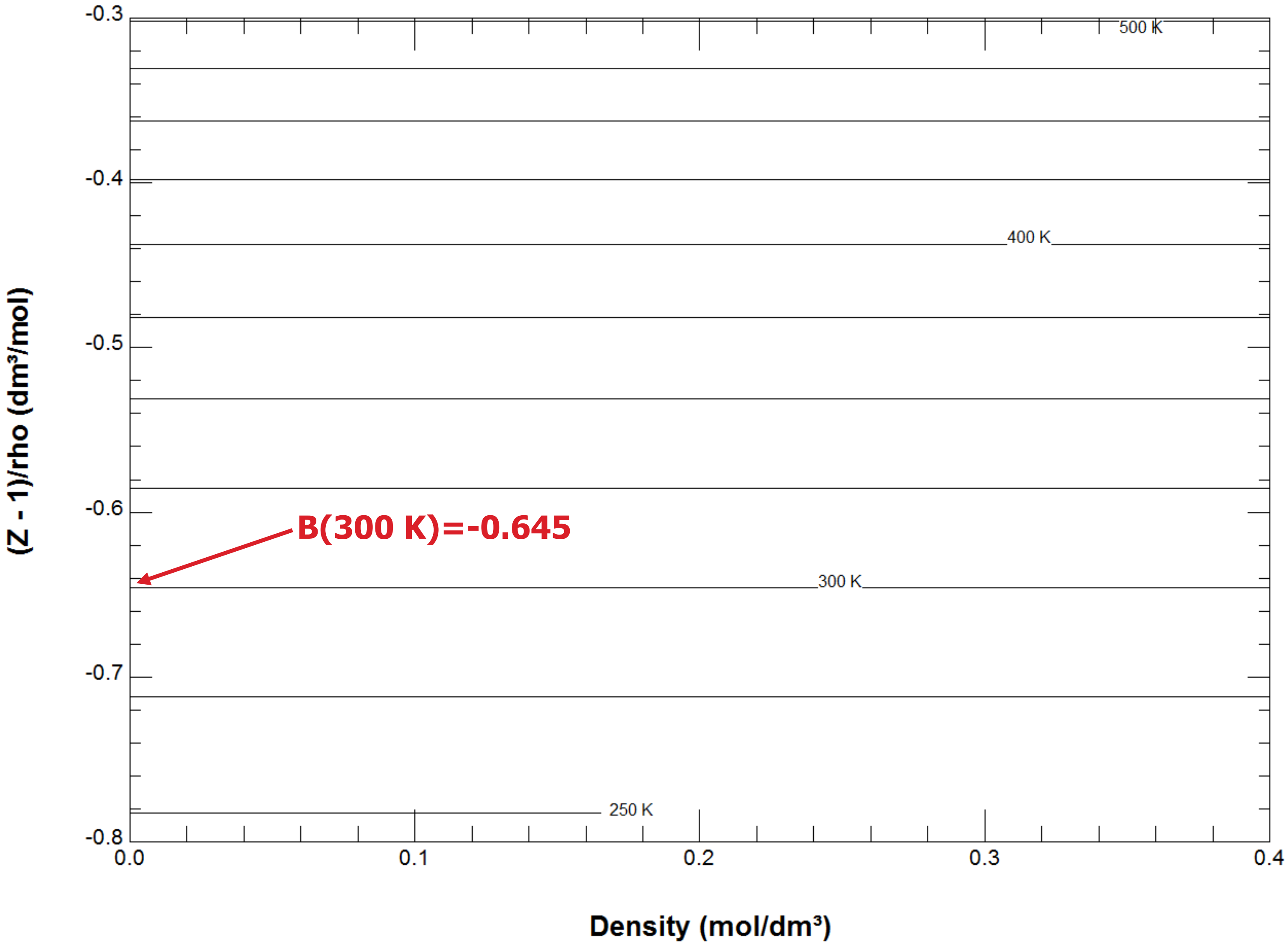
B → Second virial coefficient

C → Third virial coefficient

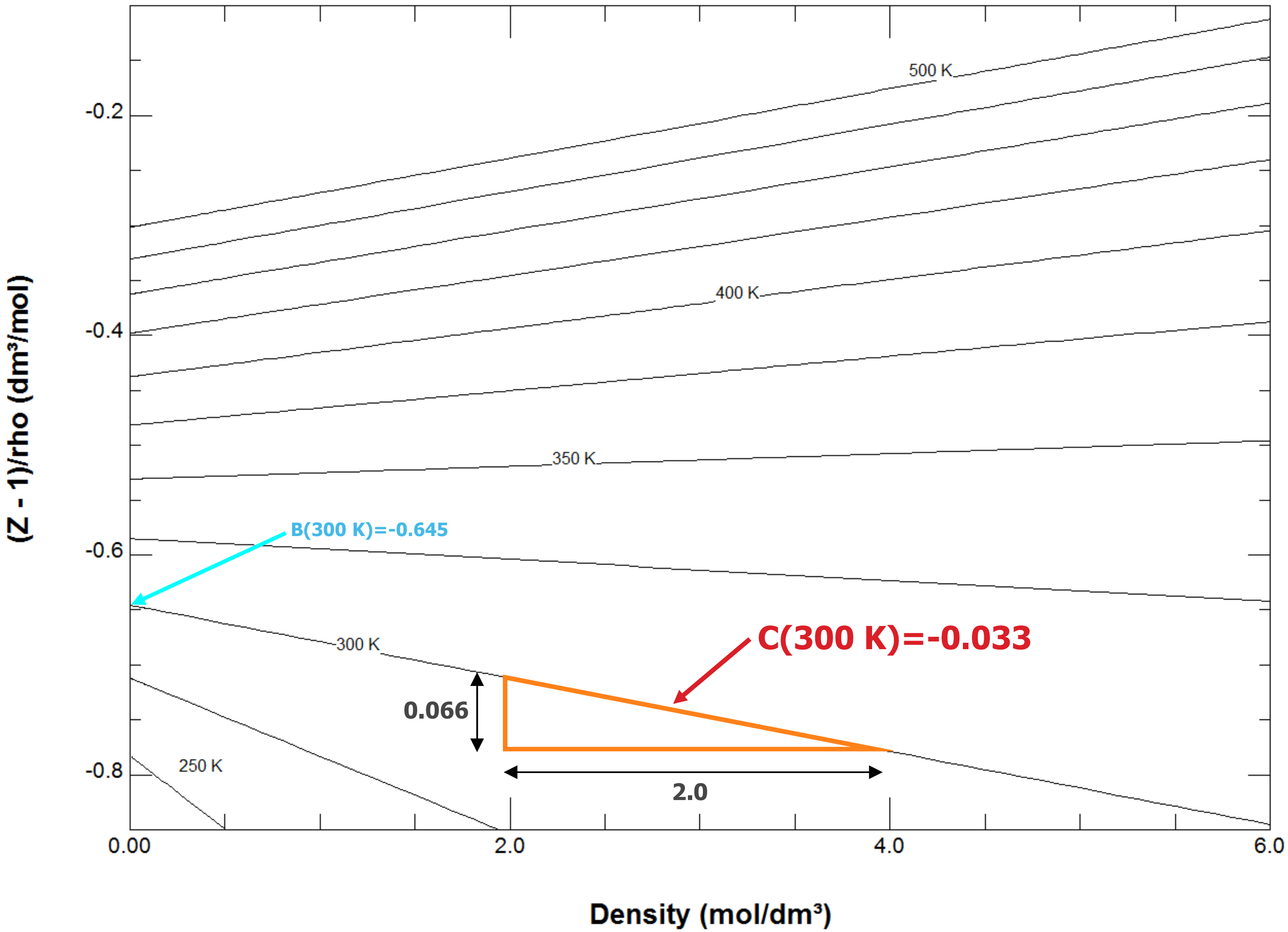
$$Z = 1 + B\rho + C\rho^2 + D\rho^3$$

$$\frac{Z-1}{\rho} = B + C\rho + D\rho^2$$

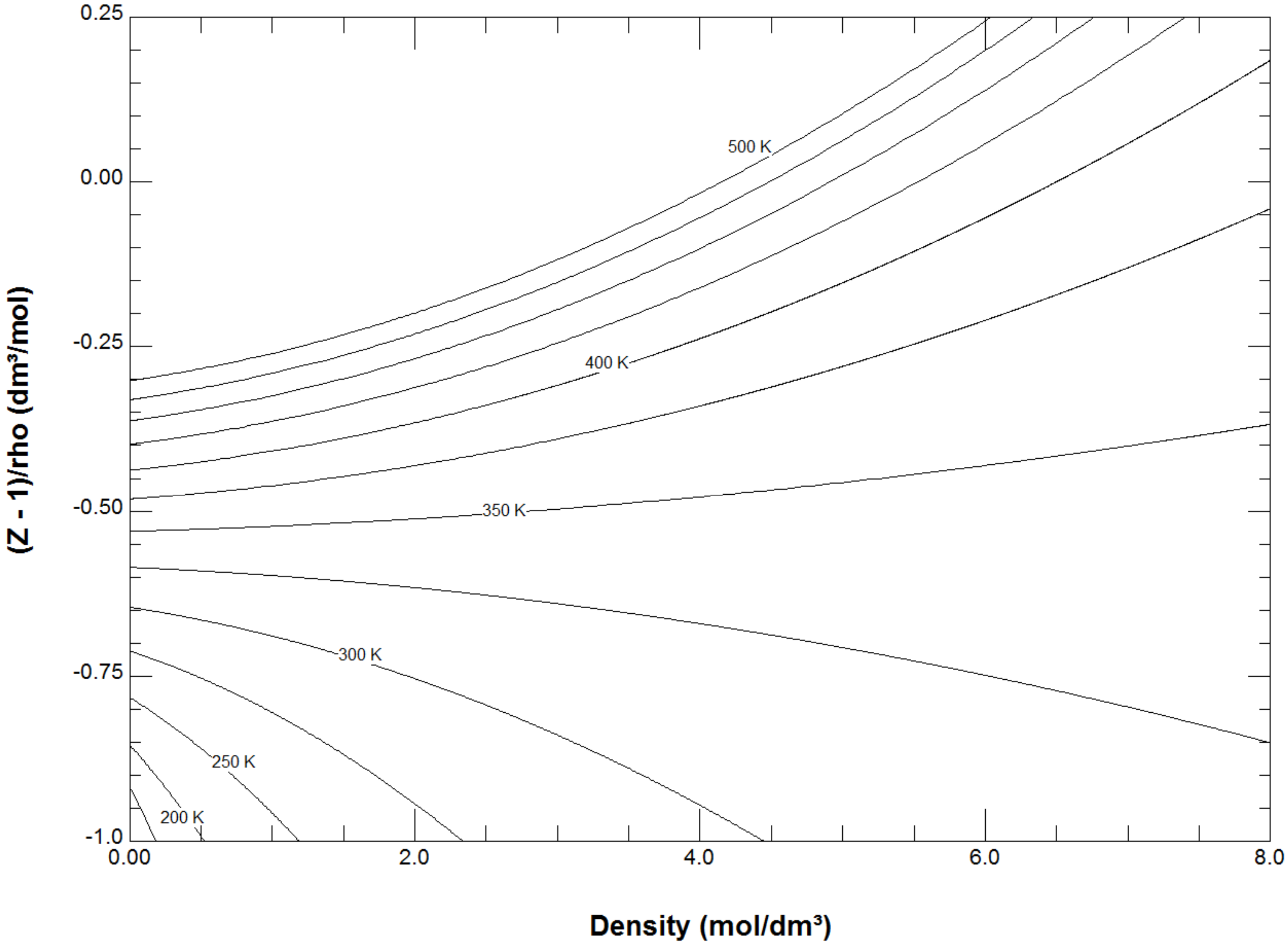
$Z = 1 + B\rho$ $(Z-1)/\rho = B$



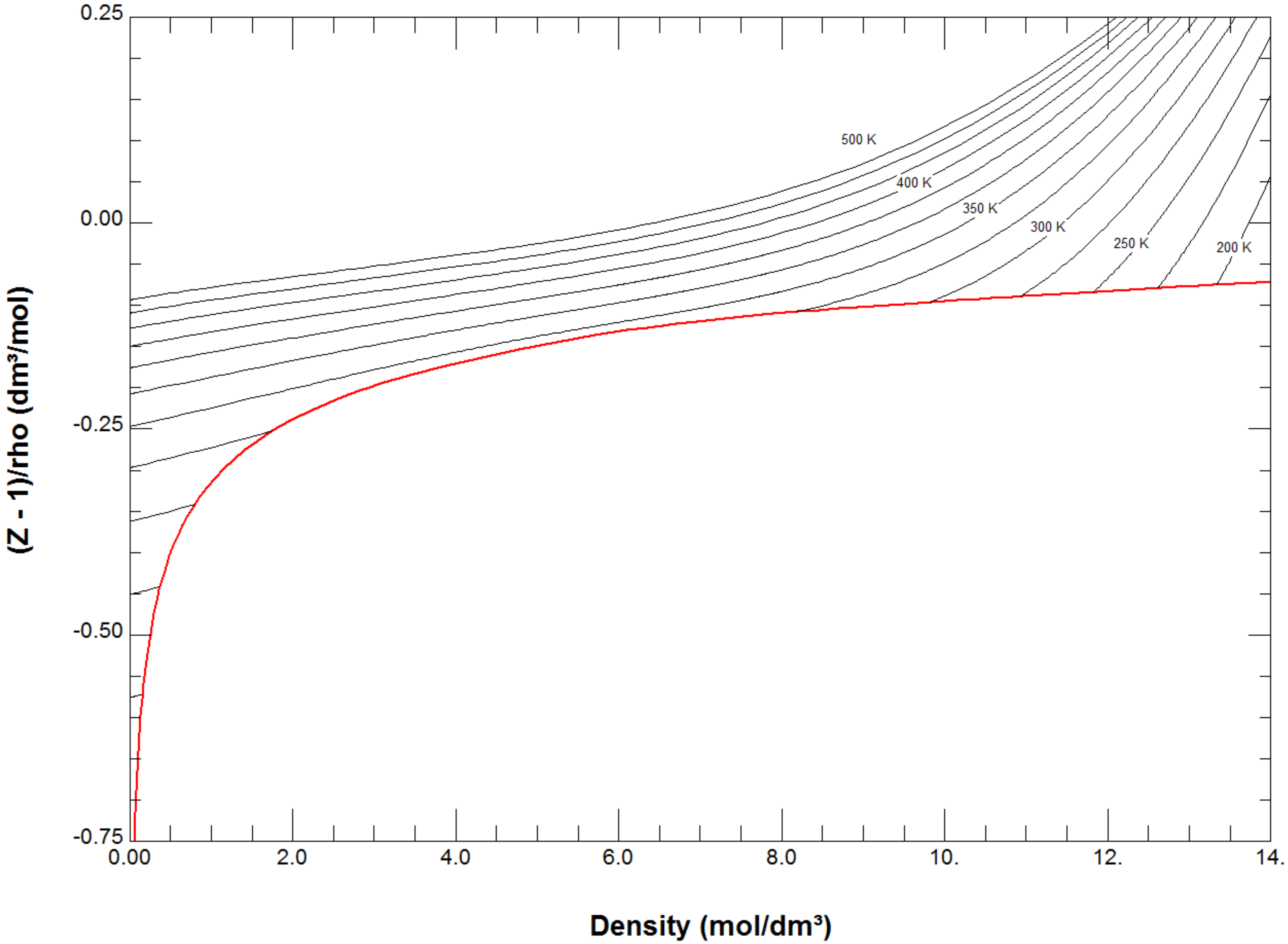
$$Z = 1 + B\rho + C\rho^2 \qquad (Z-1)/\rho = B + C\rho$$



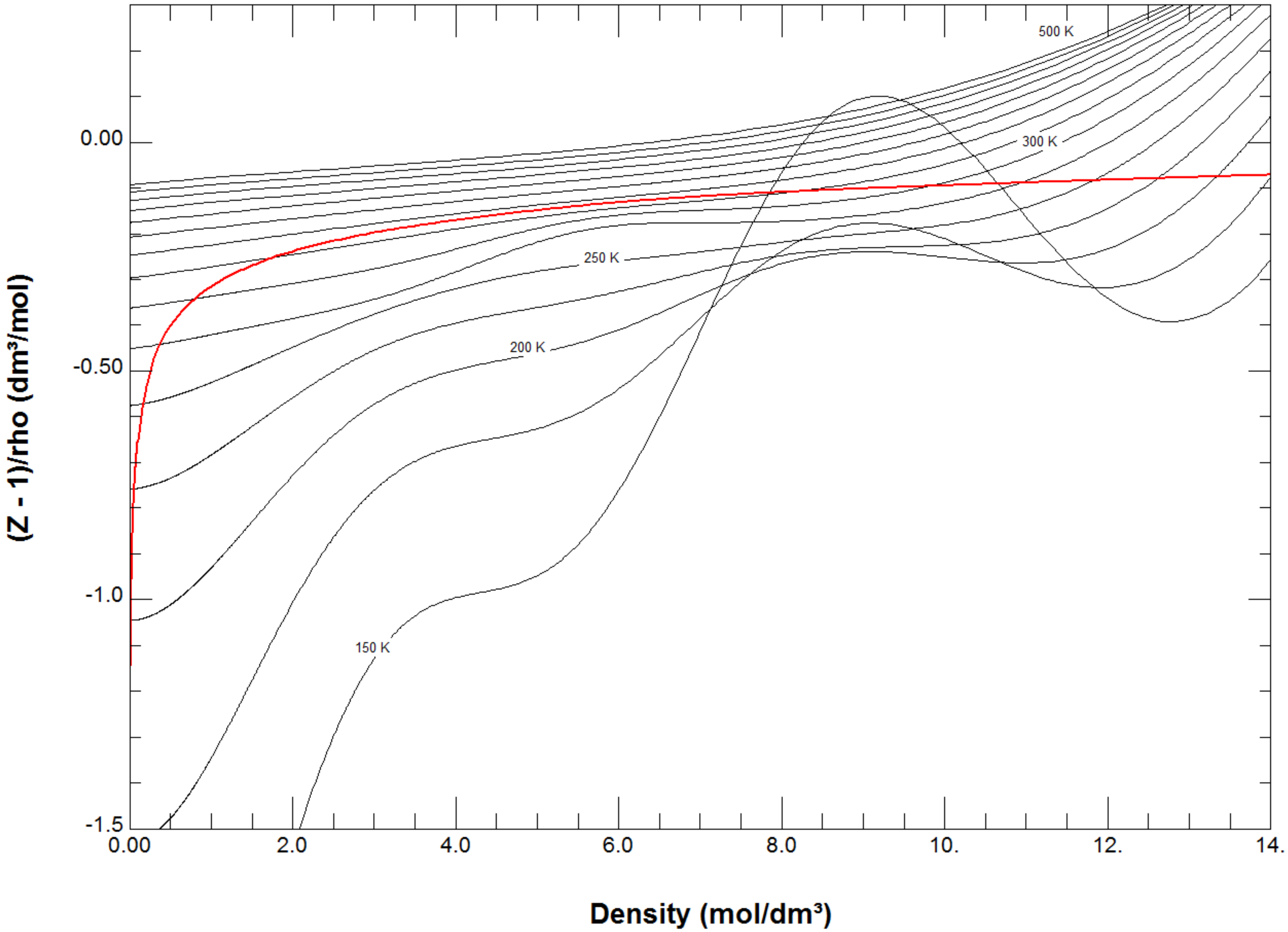
$Z=1+B\rho+C\rho^2+D\rho^3$



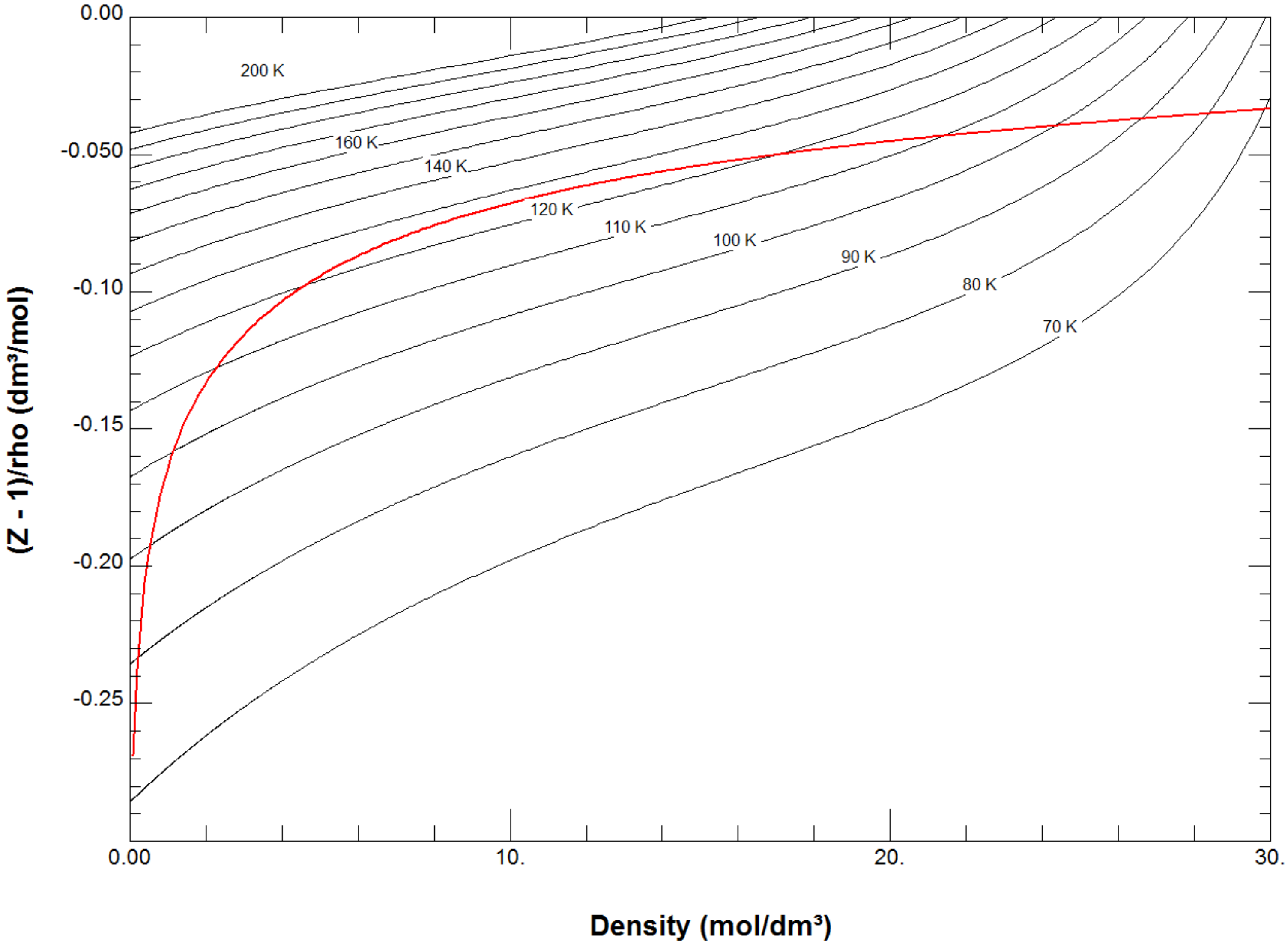
Full Equation of State – R-125



Full Equation of State – R-125



Peng-Robinson EOS for Nitrogen



Equations of State

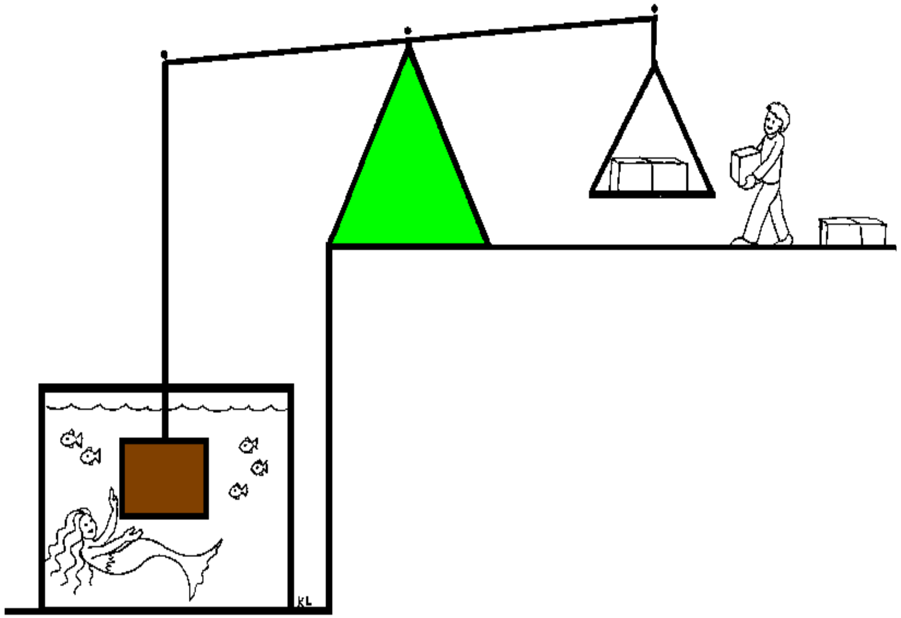
- Why not just use pressure for the independent variable in our equation of state?

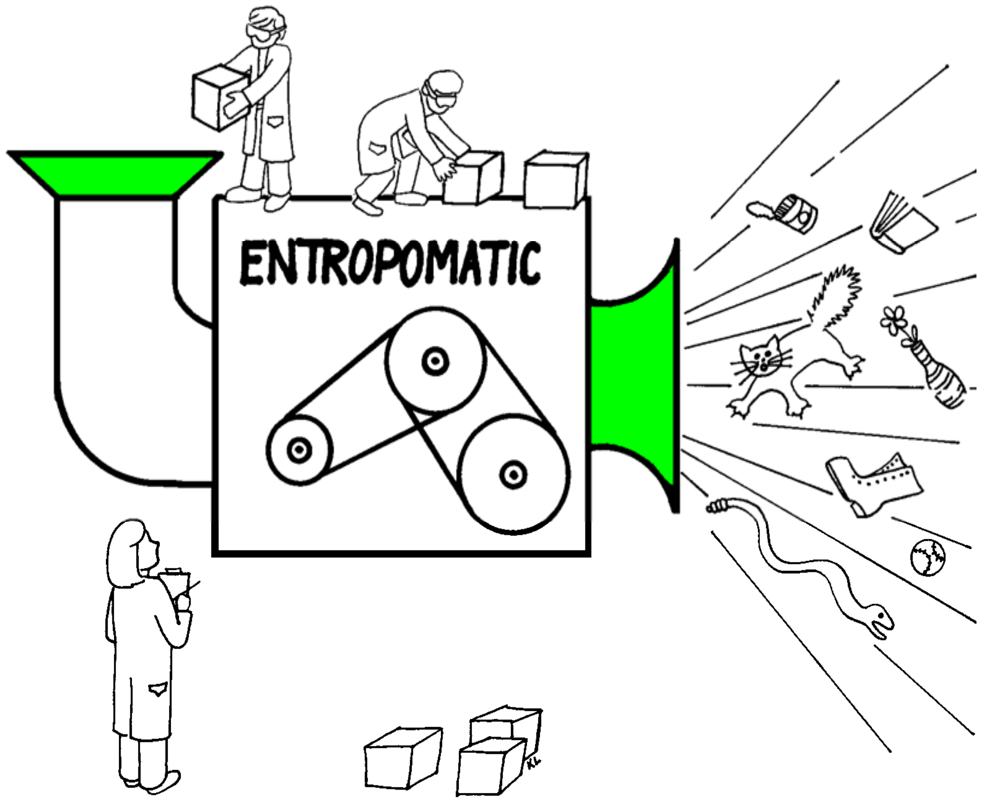
$$u = -RT^2 \frac{\partial \alpha^0}{\partial T} + RT^2 \frac{\partial \left(\ln \rho - \frac{1}{RT} \int \frac{p}{\rho^2} \partial \rho \right)}{\partial T}$$

Types of Fundamental Equations

All thermodynamic properties can be calculated as derivatives from each of the four fundamental equations:

- **Internal energy as a function of density and entropy**
  - **Entropy is not a measurable quantity.**

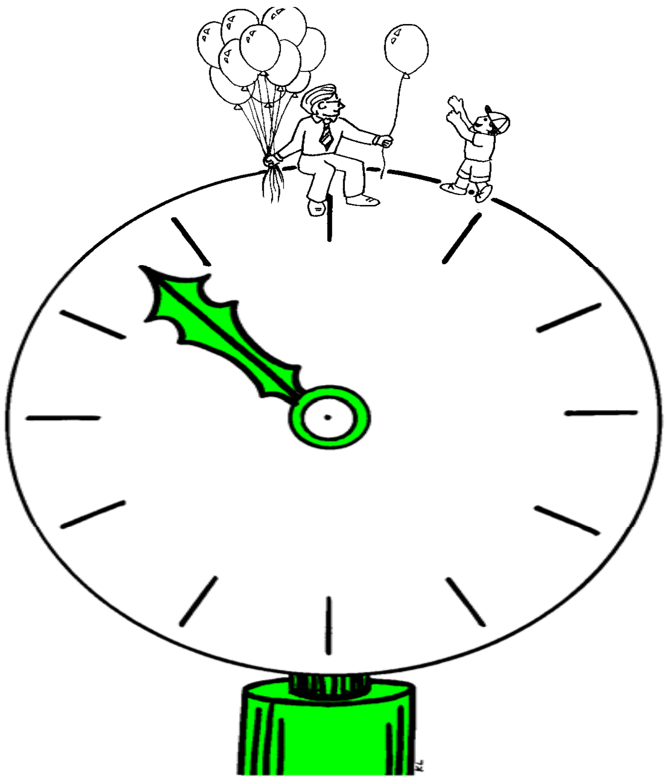


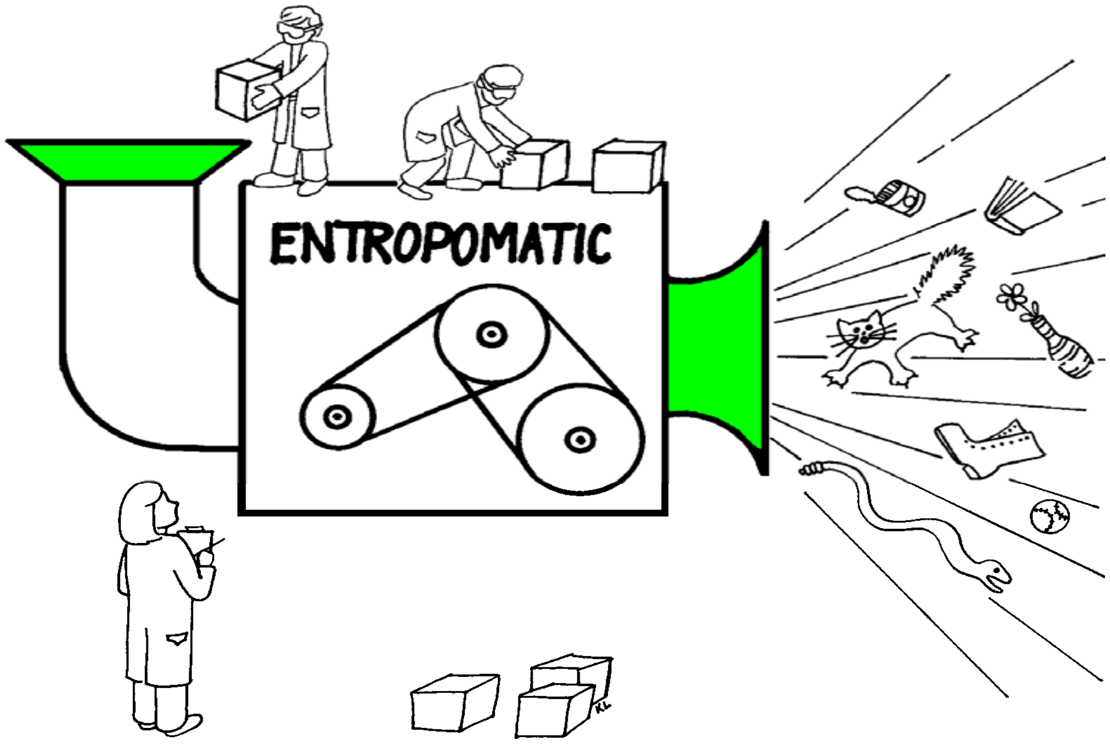


Types of Fundamental Equations

All thermodynamic properties can be calculated as derivatives from each of the four fundamental equations:

- **Enthalpy as a function of pressure and entropy**
  - **Entropy is not a measurable quantity. Is not continuous from liquid to vapor states.**

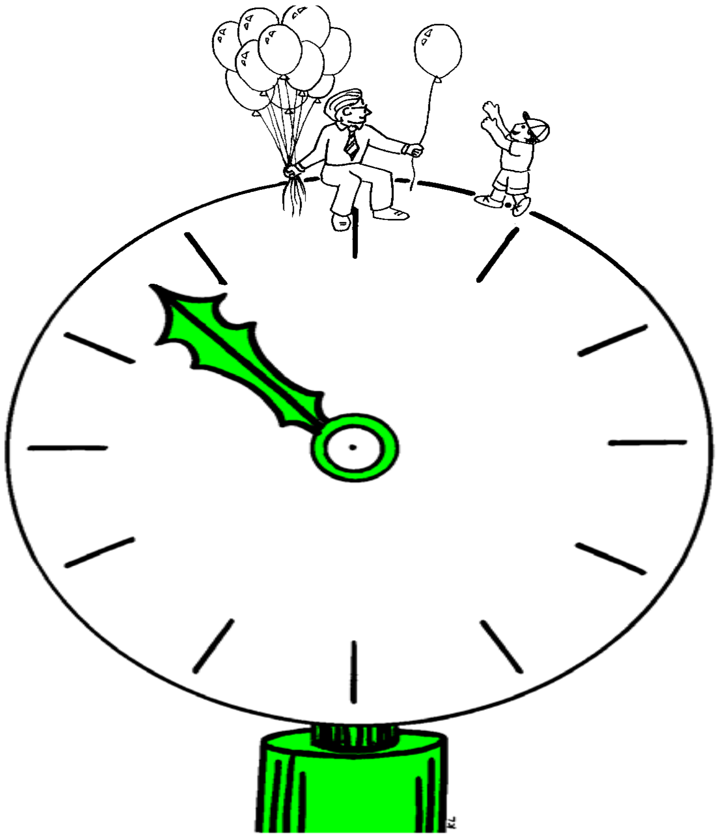


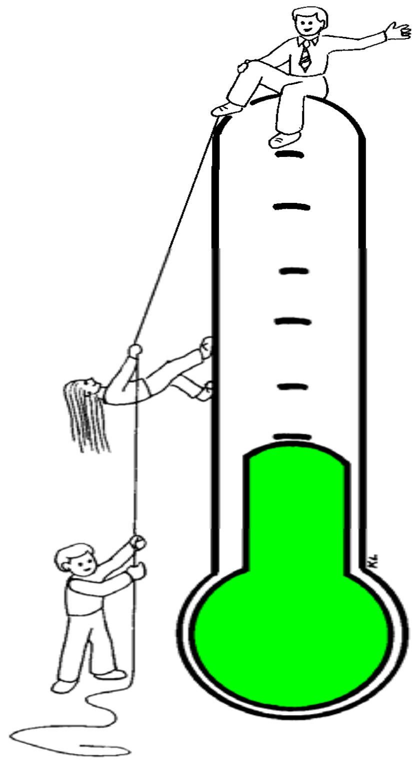


Types of Fundamental Equations

All thermodynamic properties can be calculated as derivatives from each of the four fundamental equations:

- Gibbs energy as a function of pressure and temperature
  - Is not continuous from liquid to vapor states.

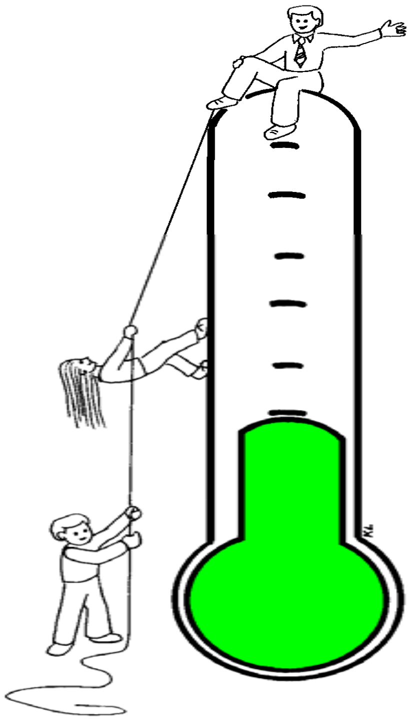


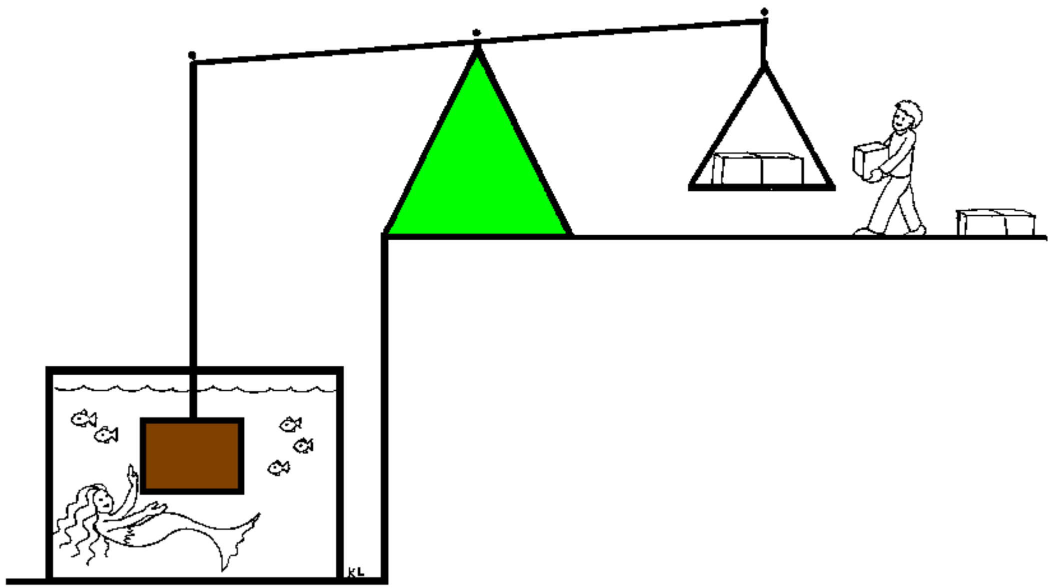


Types of Fundamental Equations

All thermodynamic properties can be calculated as derivatives from each of the four fundamental equations:

- Helmholtz energy as a function of temperature and density
  - Both temperature and density are measurable. Continuous across two-phase region.





Why the Helmholtz Energy is Best

$$p = \rho^2 \frac{\partial a}{\partial \rho}$$

$$s = -\frac{\partial a}{\partial T}$$

$$u = a - T\frac{\partial a}{\partial T}$$

Who is Helmholtz?

Hermann Ludwig Ferdinand von Helmholtz (1821 – 1894)

Helmholtz Energy Equation of State

$\delta = \rho / \rho_{\text{crit}} \qquad \tau = T_{\text{crit}} / T$ **Reduced independent variables**

$\alpha = \alpha^{\text{ideal}}$ **Ideal gas**

$+ \sum N_i \tau^{t_i} \delta^{d_i}$ **Polynomial terms**

$+ \sum N_j \tau^{t_j} \delta^{d_j} \exp\left(-\delta^{l_j}\right)$ **Polynomial+exponential terms**

$+ \sum N_k \tau^{t_k} \delta^{d_k} \exp\left(-a_k (\delta - \varepsilon_k)^2 - \beta_k (\tau - \gamma_k)^2\right)$

Gaussian bell-shaped terms

$$p = RT\rho \left[1 + \frac{\partial \alpha^{\text{r}}}{\partial \delta} \right]$$

$$C_V = R \left[-\tau^2 \frac{\partial^2 \alpha}{\partial \tau^2} \right]$$

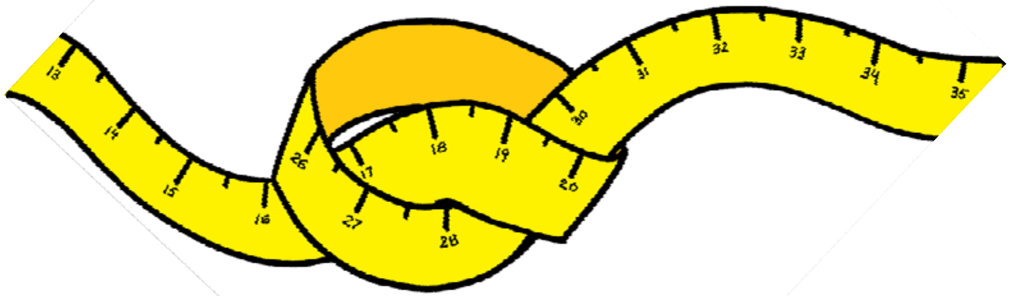
Other properties as derivatives only

Data Needed for Fitting Equations of State

- Ideal gas heat capacity data
- Pressure-density-temperature data
- Vapor pressure data
- Speed of sound data
- Heat capacity data
- Virial coefficients
- etc.

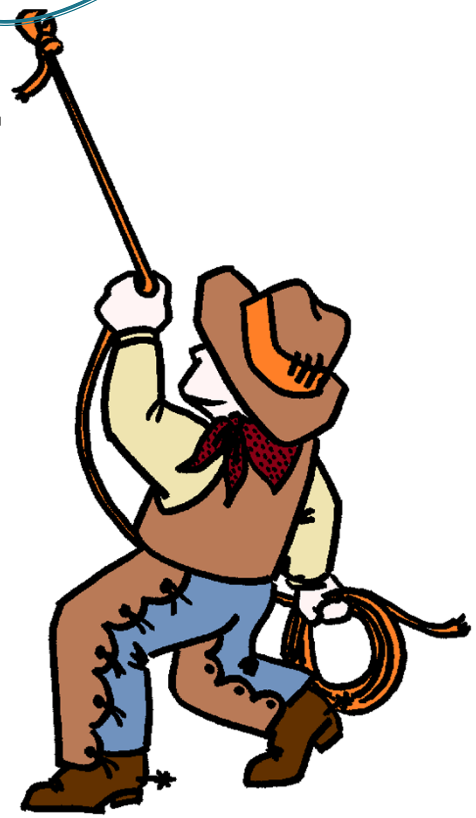
Typical Data Available

- Reference equations of state with very low uncertainties are available for the few but well characterized fluids.
- A number of fluids have adequate data to make good equations, and most of these have been published.
- The rest have little or no data above the critical point, and often no PVT data in the vapor phase.
  - Extrapolation without constraints and visual observations will lead to poor equations.
- In all cases, even the most well measured substances can go astray at very high densities.

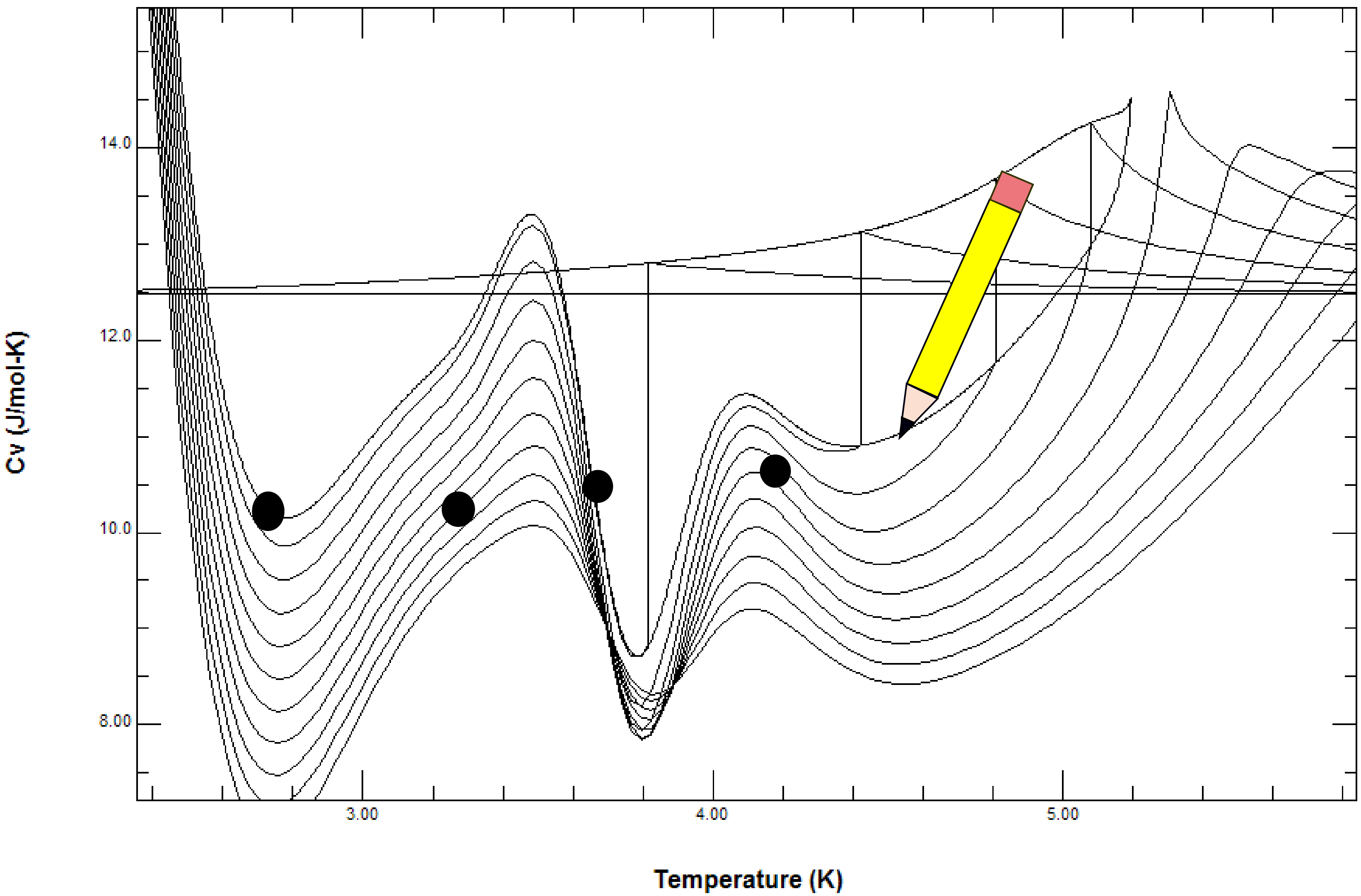


History of Equations of State

- Linear fitting of data only with a bank of terms – no graphical examination of behavior.
- Same linear fitting of data but with graphical inspection of equation – bad extrapolation fixed with "graphite research".
- Combination of linear and nonlinear fitting.
- Pure nonlinear fitting of data only (with graphical assessment of extrapolation).
- Nonlinear fitting combined with multiple constraints to control curvature of different properties.

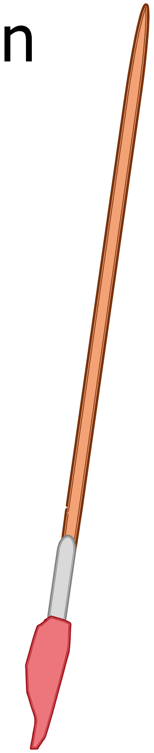


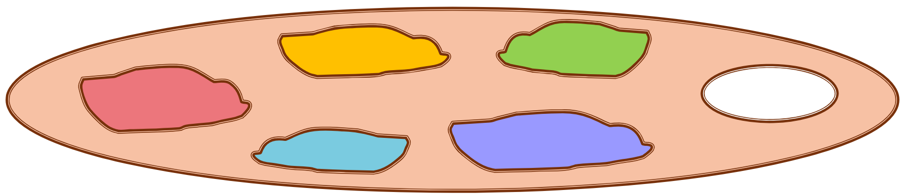
Graphite Research



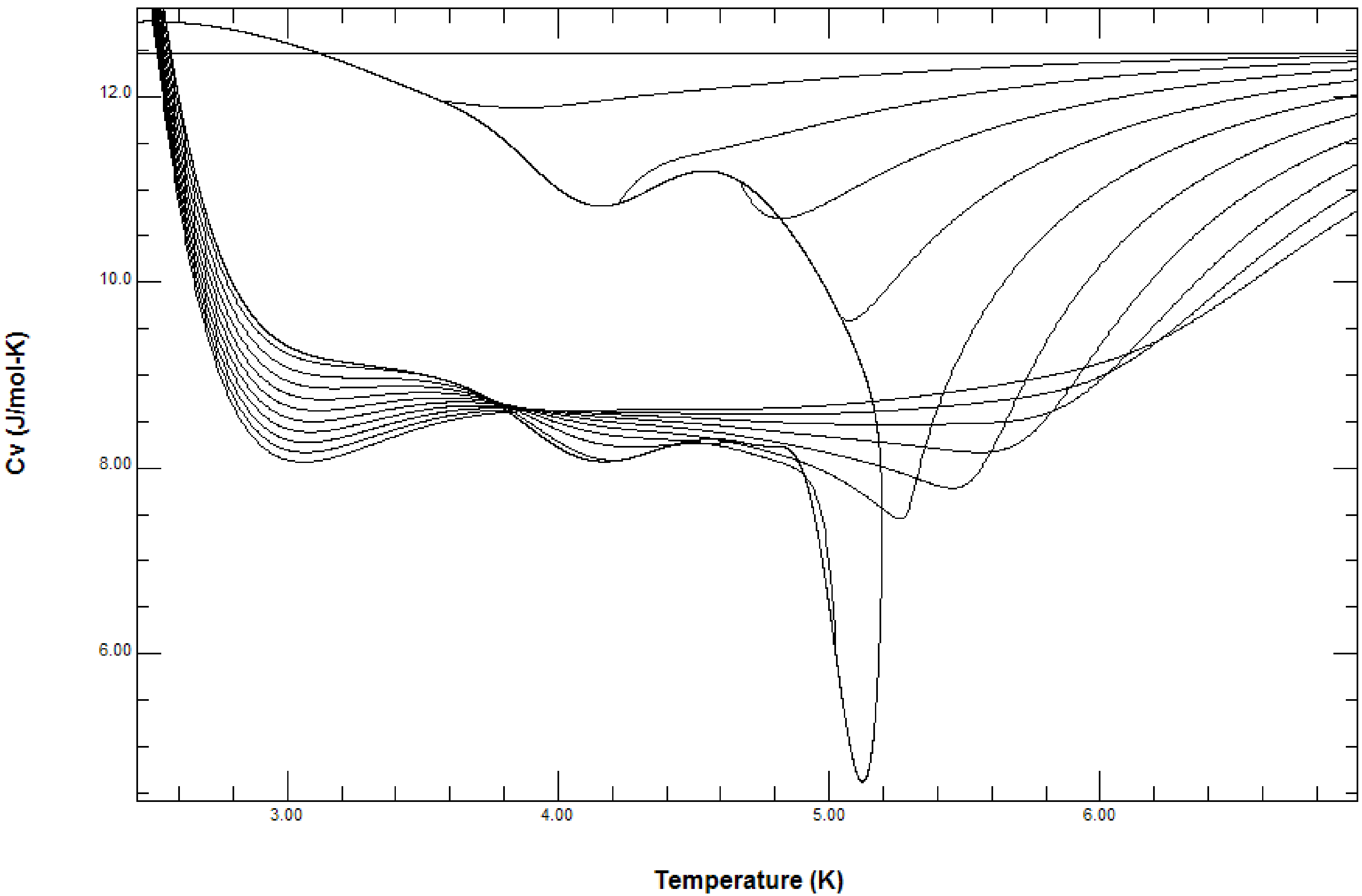
Fitting: Art vs. Statistics

- Early fitting programs only looked at statistics.
- Modern functional forms are extremely flexible and can fit any kind of data – good or bad.
- The statistics can show that an equation does a wonderful job fitting the good (and bad) data, but only a full inspection of the behavior of the equation will validate its accuracy.
- The correlator must have good knowledge of the behavior of a fluid to remove bad performance, becoming an Artist by "painting" the fluid's shape.

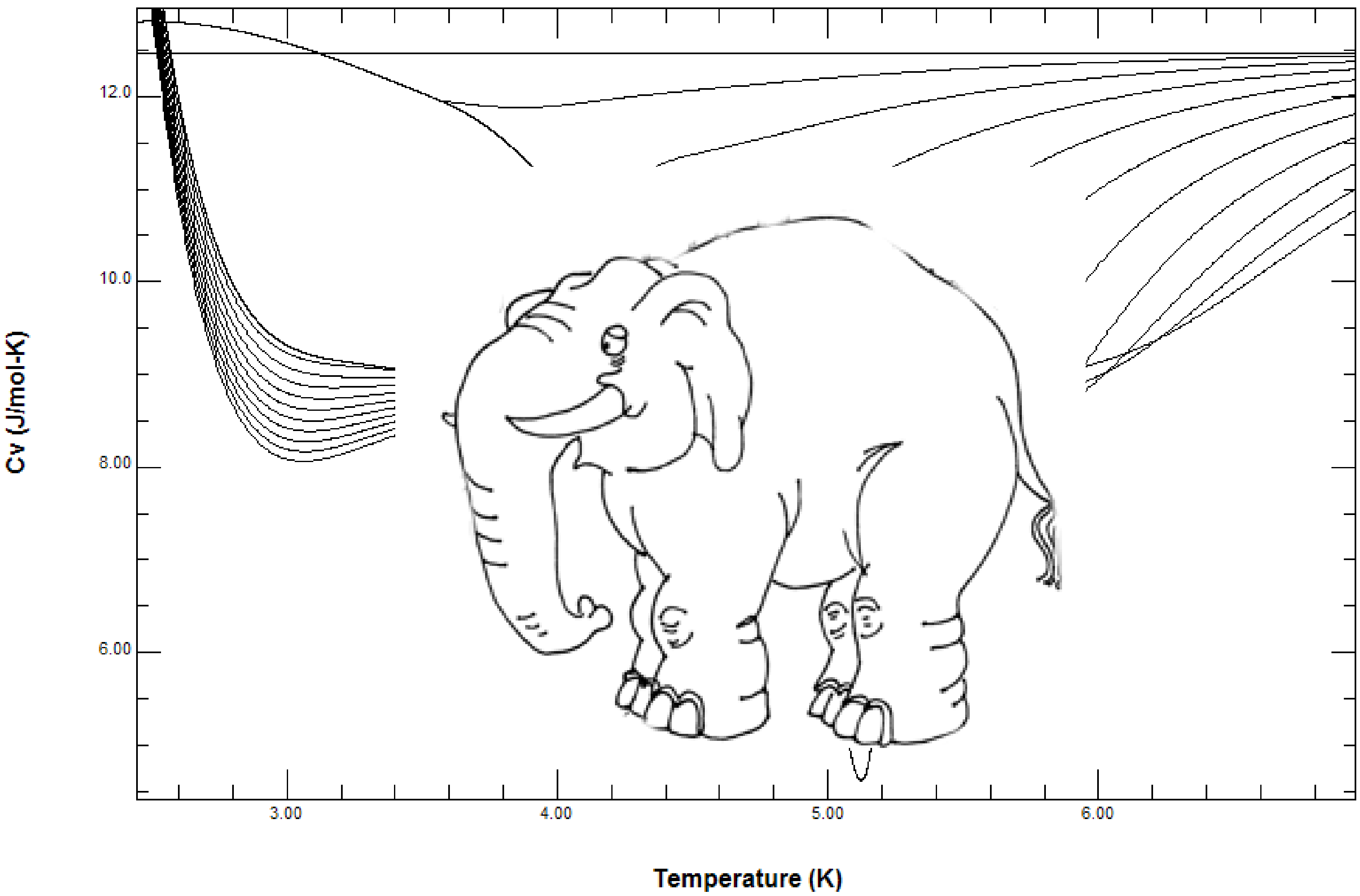




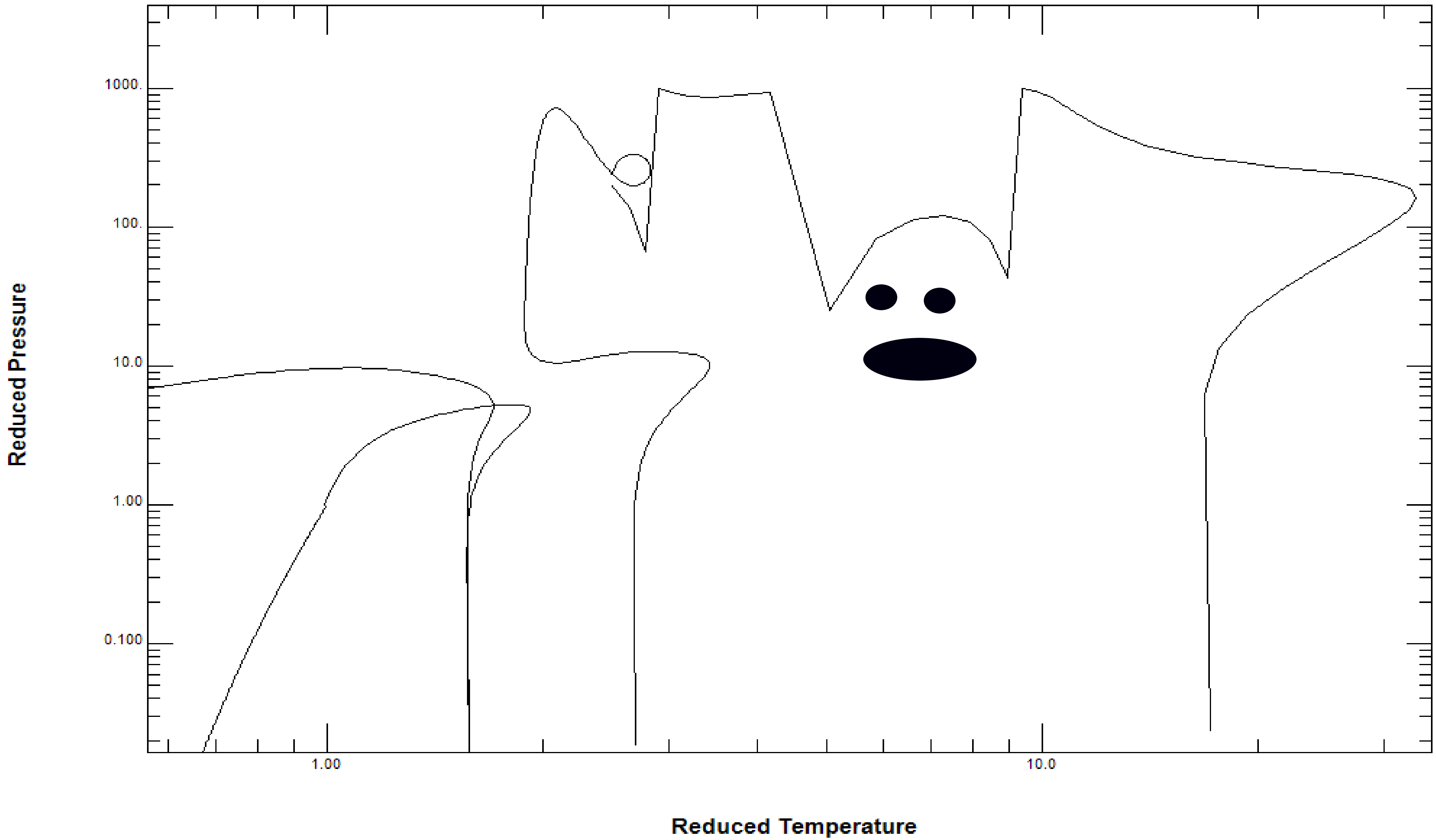
Fitting Equations of State IS an Art



Fitting Equations of State IS an Art

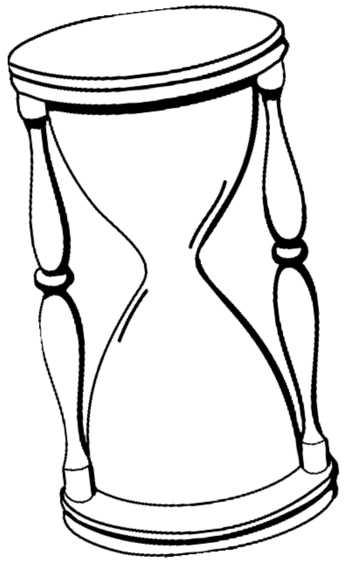


Sometimes you can even see ghosts…

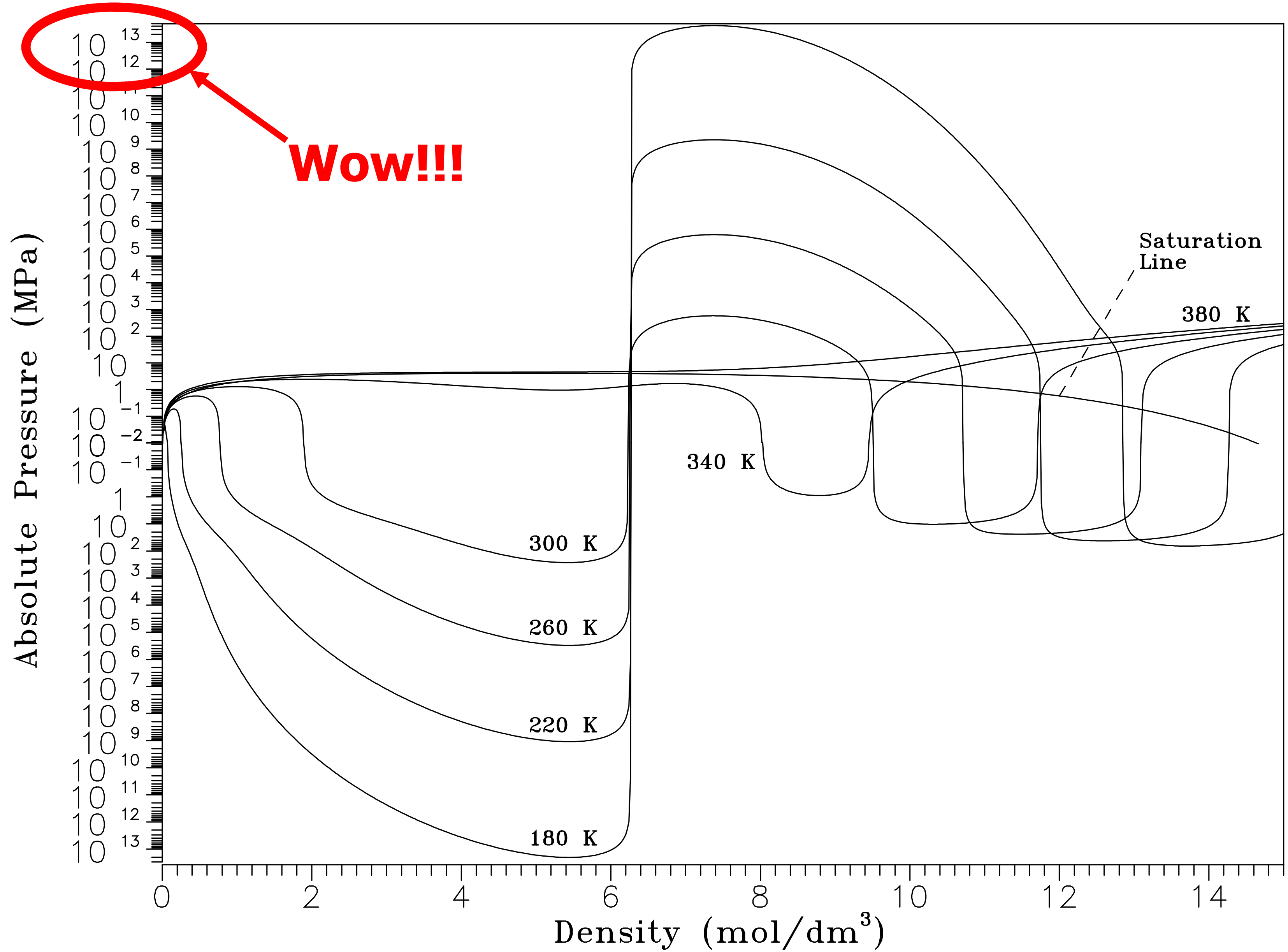


Techniques Used in Fitting

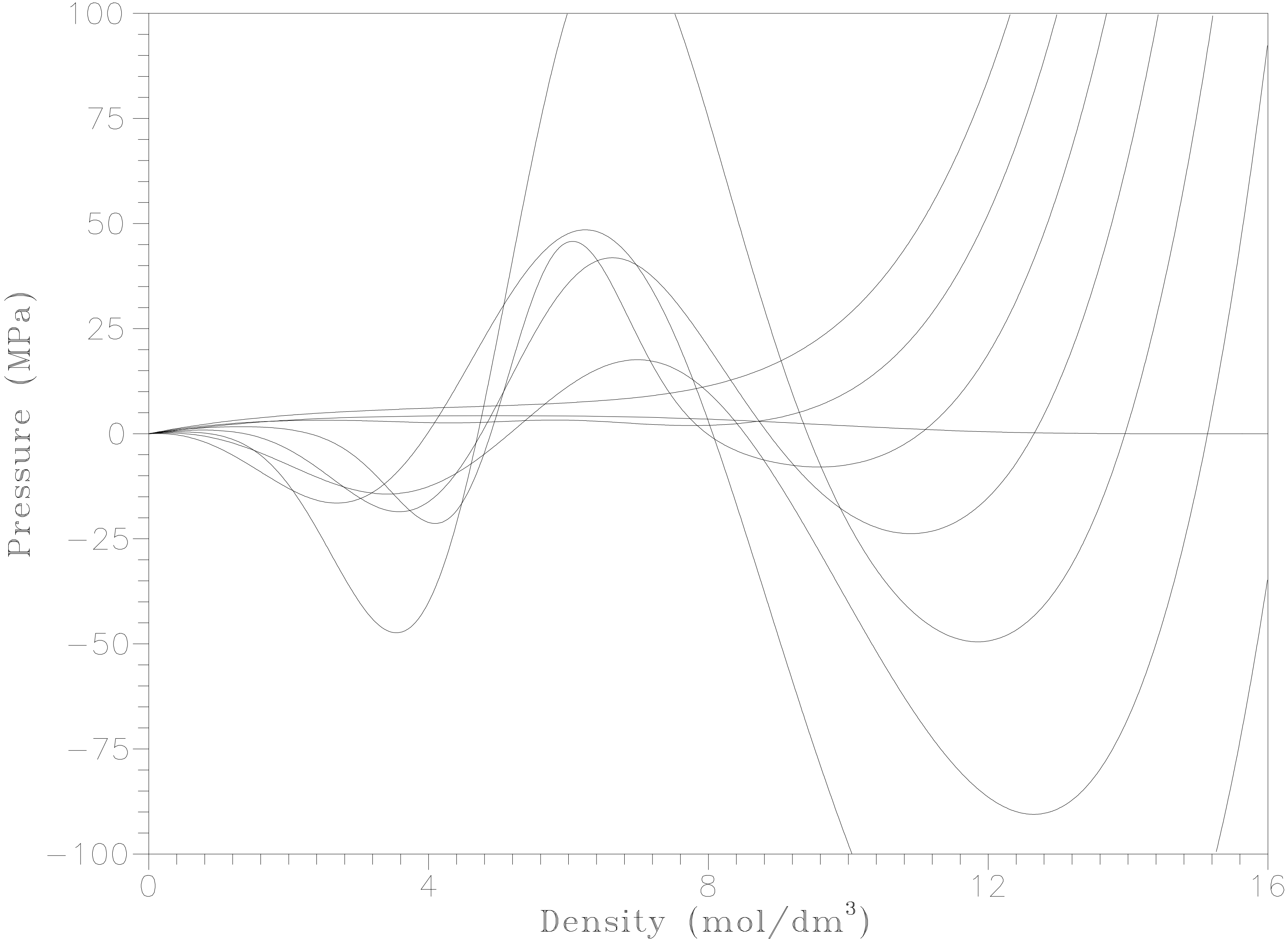
- Linear fitting
  - Fast.
  - Selects optimum terms from a large bank.
  - Can fit multiple properties simultaneously, but isobaric heat capacity, sound speed, and phase boundary data must be linearized with a preliminary equation.
  - Final equations have 25-50 terms.
- Nonlinear fitting
  - Very time consuming.
  - Can fit multiple properties simultaneously without the need to linearize.
  - Final equations have 15-25 terms.



R-134a


Wow!!!
Absolute Pressure (MPa)
Density (mol/dm3)
0
2
4
6
8
10
12
14
Saturation Line
380 K
340 K
300 K
260 K
220 K
180 K

Propane

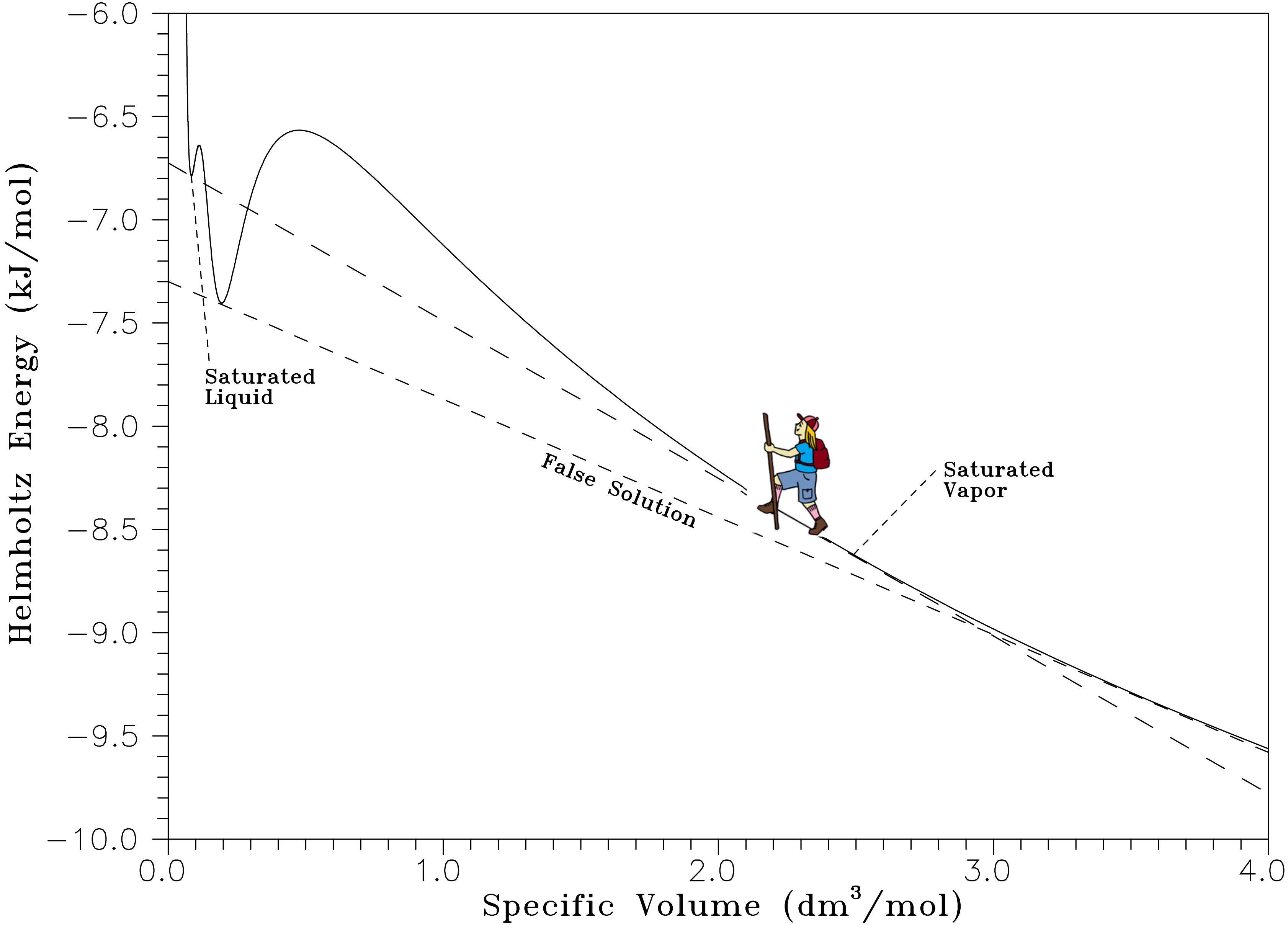


100
75
50
25
0
−25
−50
−75
−100
Pressure (MPa)
0
4
8
12
16
Density (mol/dm³)

Nonlinear Fitting

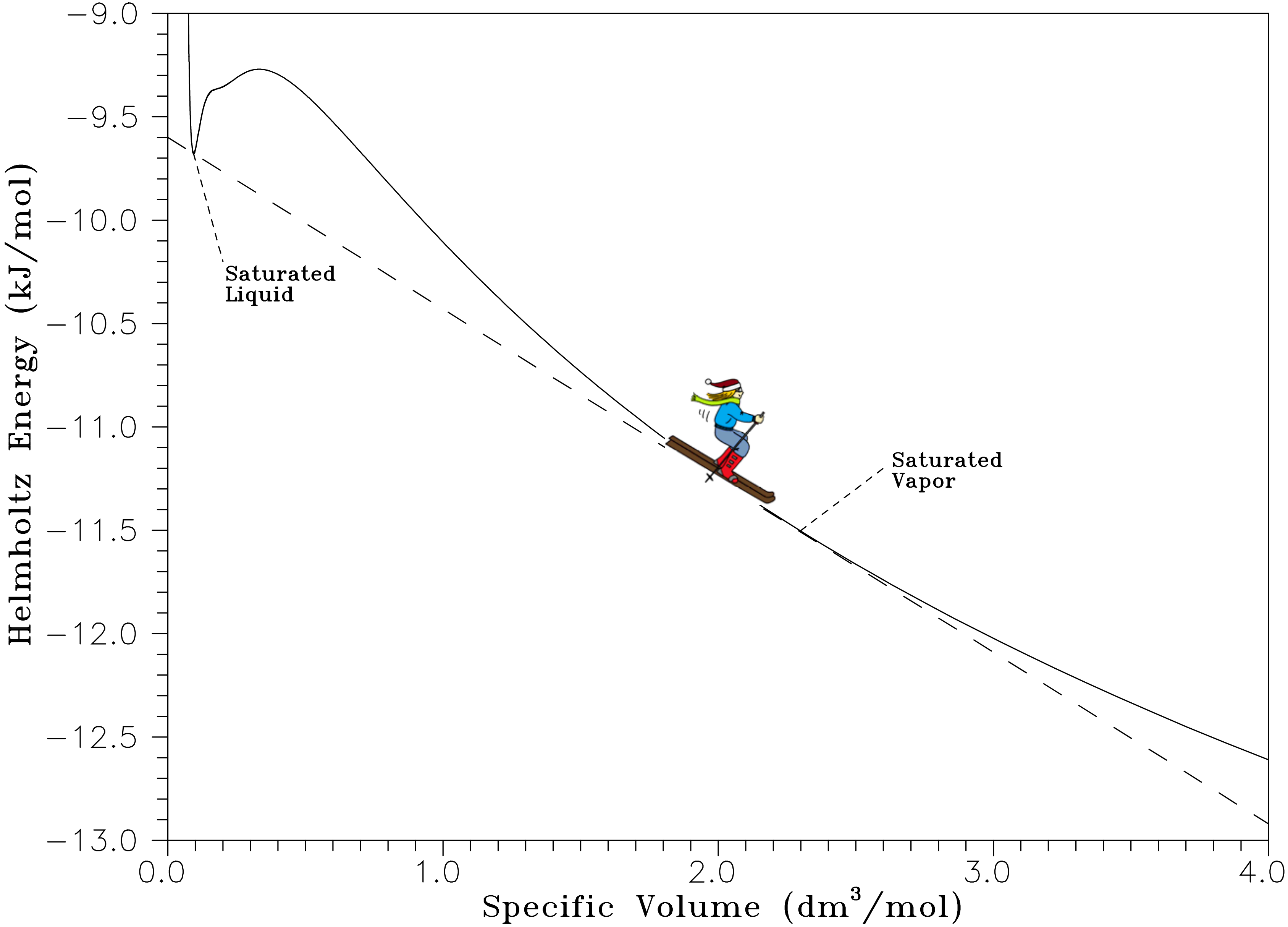
- Nonlinear fitting can include the exponents on density and temperature, as well as the coefficients and exponents within the Gaussian-bell shaped terms.
- Nonlinear fitting can use greater than and less than concepts to shape an equation in the absence of data, such as:
  - Make c_v increase in value as temperature drops to low values in the liquid phase.
  - Force a temperature exponent to be less than a particular value.
  - Keep the critical density or temperature within a set bound (when it is fitted).
  - Calculate the rectilinear diameter and keep it straight (no curvature).
  - Smooth out the ideal curves.

R-143a



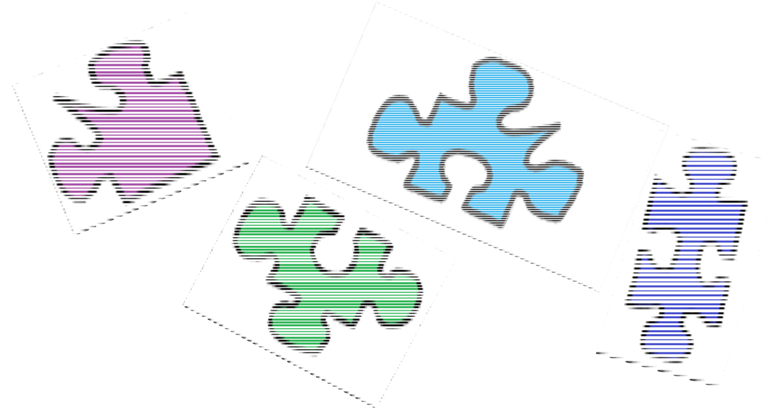
−6.0
−6.5
−7.0
−7.5
−8.0
−8.5
−9.0
−9.5
−10.0
Helmholtz Energy (kJ/mol)
0.0
1.0
2.0
3.0
4.0
Specific Volume (dm³/mol)
Saturated Liquid
Saturated Vapor
False Solution

R-125



−9.0
−9.5
−10.0
−10.5
−11.0
−11.5
−12.0
−12.5
−13.0
Helmholtz Energy (kJ/mol)
0.0
1.0
2.0
3.0
4.0
Specific Volume (dm³/mol)
Saturated Liquid
Saturated Vapor

Fitting Constraints



CV/DT/S+

- Property held constant
- Property to shape
- Property varied

What to do with the derivative:

- + Make it positive
- – Make it negative
- 0 Make it zero
- & Allow only one cross from negative to positive

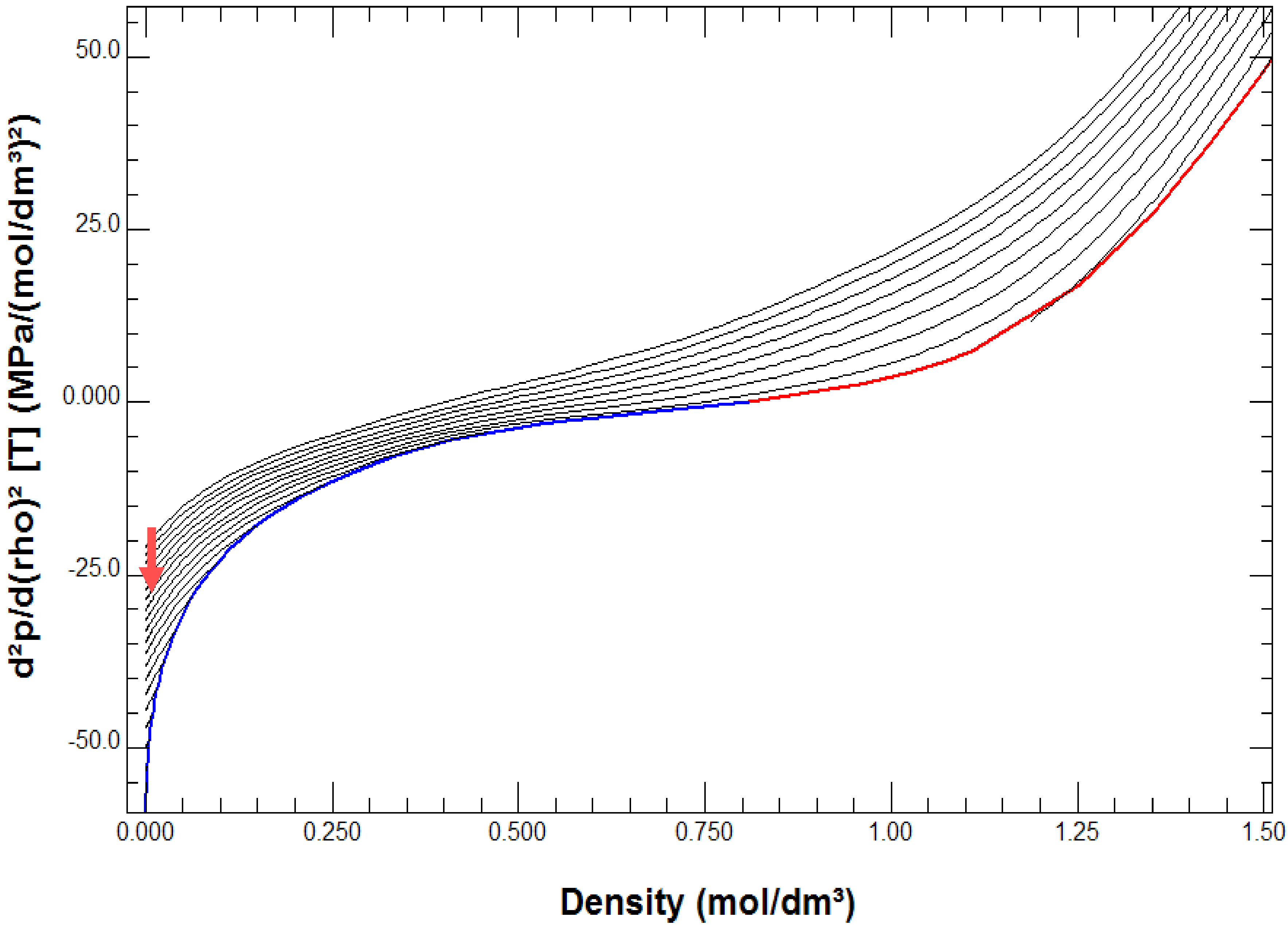
Derivative to fit

Can be one of four:

- S – Slope
- C – Curvature
- 3 – 3rd derivative
- 4 – 4th derivative

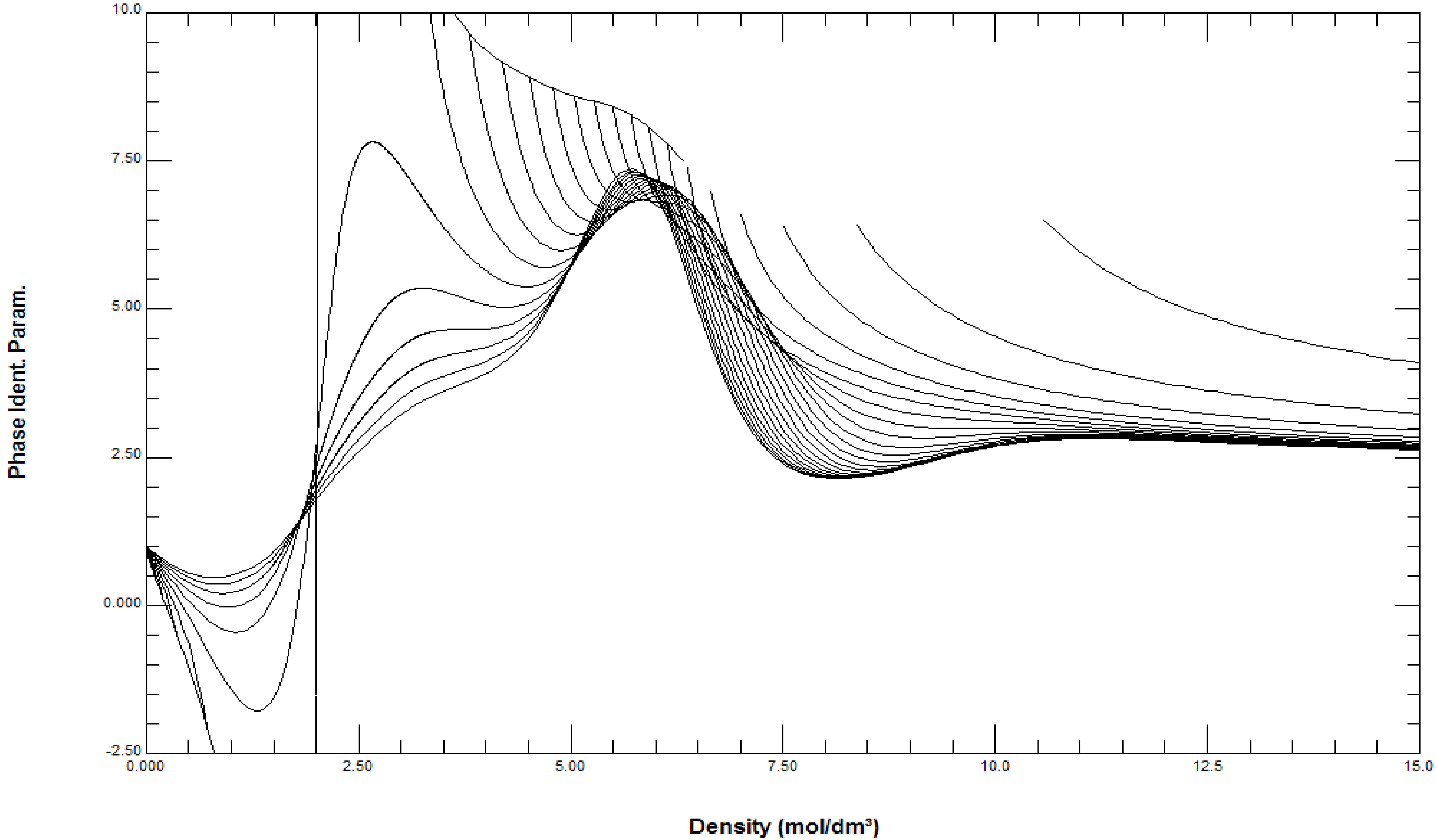
Constraint Examples

- 2PD/ST/A-+ — Make the second derivative along the saturation line have a negative slope, positive curvature, negative 3rd, and positive 4th .
- C/DL/A& — Calculate C on a log temperature scale, allowing each derivative to pass through zero once only.
- CV/ST/A+ — Keep all derivatives of Cv along the saturation line positive.
- JI/TD/C0 — Keep the curvature along the Joule Inversion curve zero as the density is increased.
- P/TD/A+ — Along an isotherm, force all pressure derivatives to be positive while varying density.
- RD/ST/C0 — Make the rectilinear diameter straight, with no curvature.
- W/ST/A- — Force the derivatives of the speed of sound to all have negative derivatives along the saturation curve.
- Z1/ST/A+- — Along the saturation line, make the derivatives (Z-1)/rho positive for the slope, negative for the curvature, positive for the 3rd, and negative for the 4th.

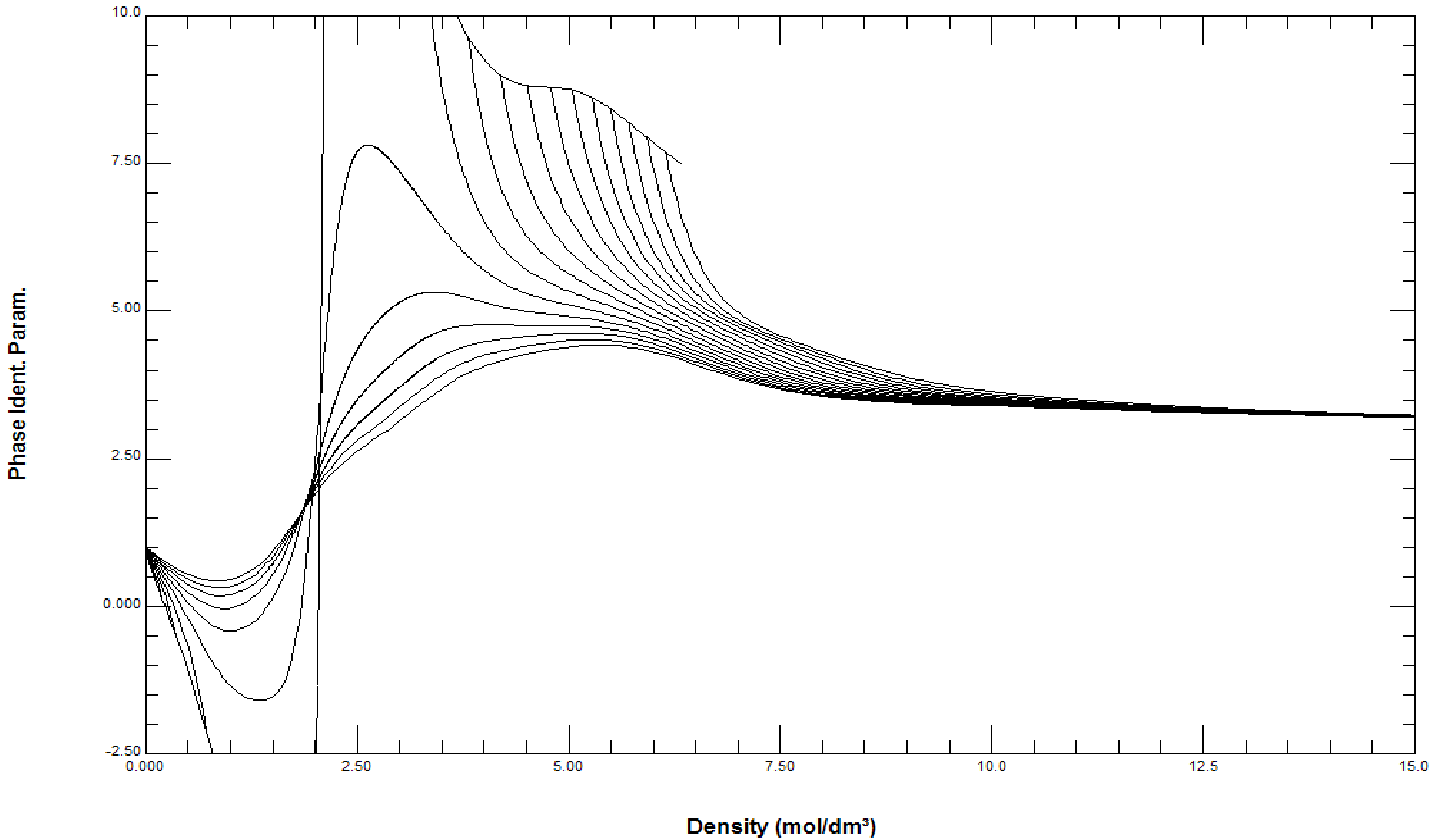


50.0
25.0
0.000
-25.0
-50.0
d²p/d(rho)² [T] (MPa/(mol/dm³)²)
0.000
0.250
0.500
0.750
1.00
1.25
1.50
Density (mol/dm³)

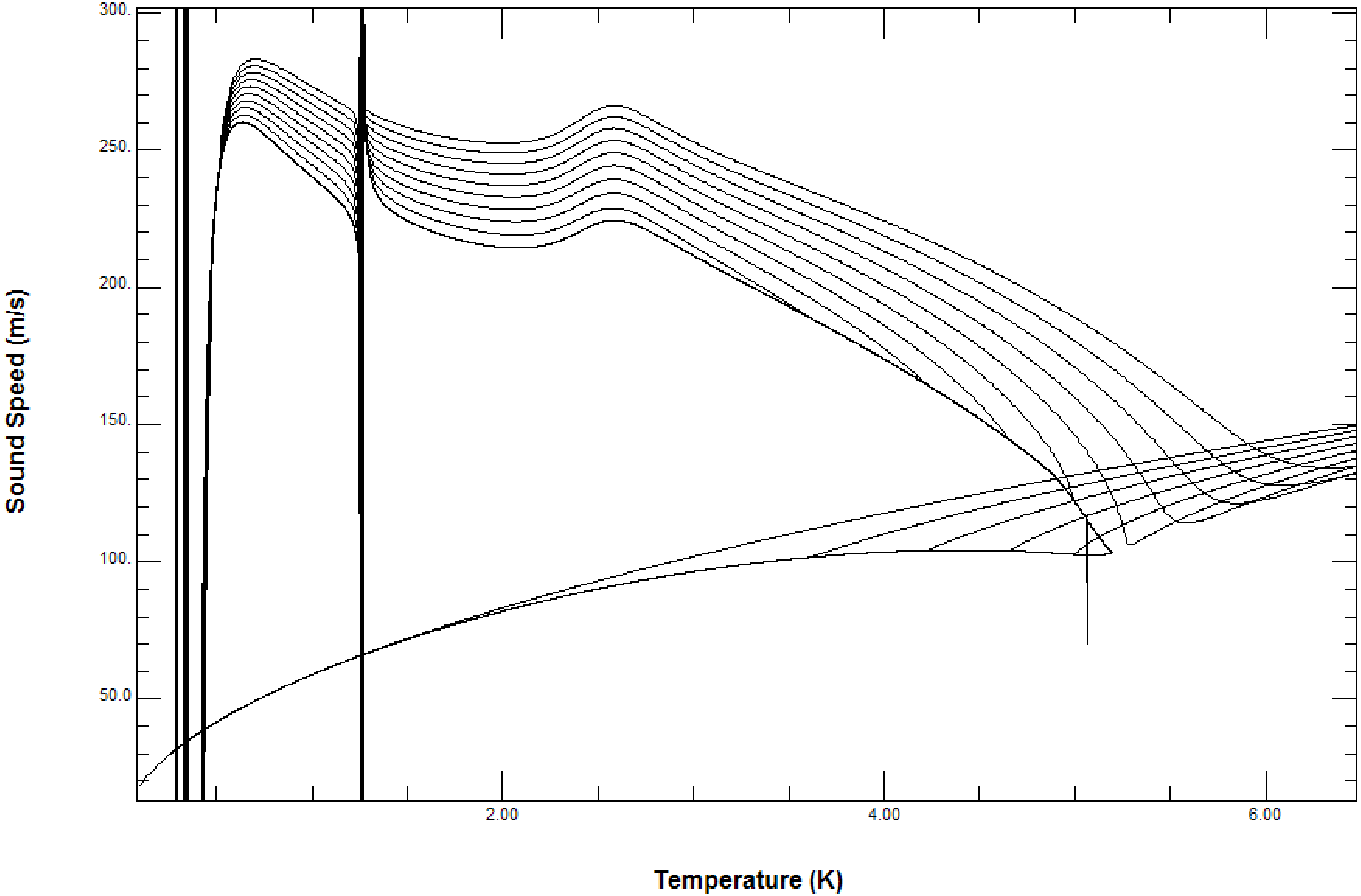
Snapshot of EOS Fitting



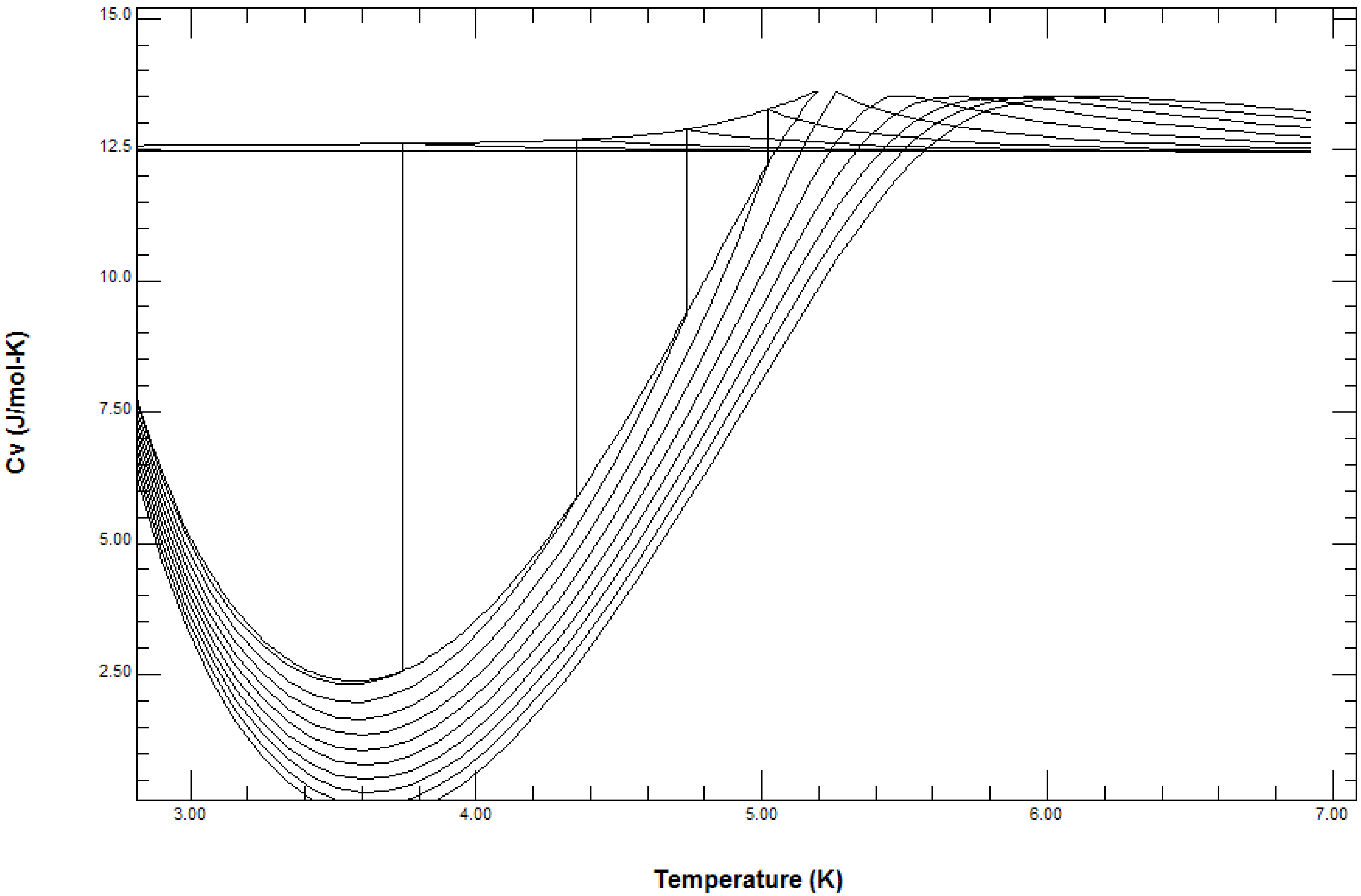
Several Hours Later with Constraints



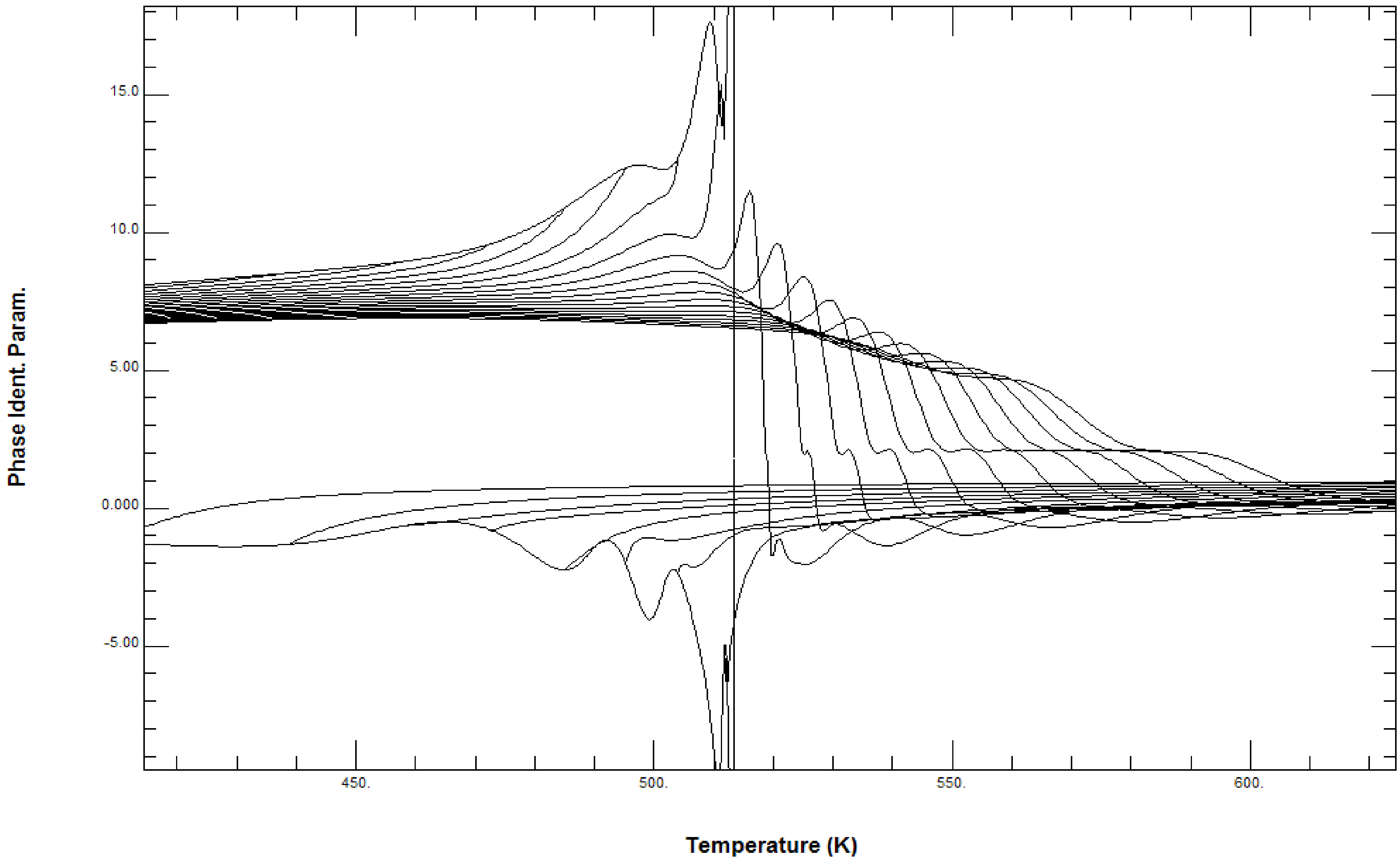
Preliminary Helium Equation



Preliminary Helium Equation



Methanol



Phase Ident. Param.
15.0
10.0
5.00
0.000
-5.00
450.
500.
550.
600.
Temperature (K)

Thermodynamic Tree

Red arrows represent a partial derivative with respect to temperature.

Blue arrows represent a partial derivative with respect to density.

Real Tree

$$A(V,T)$$

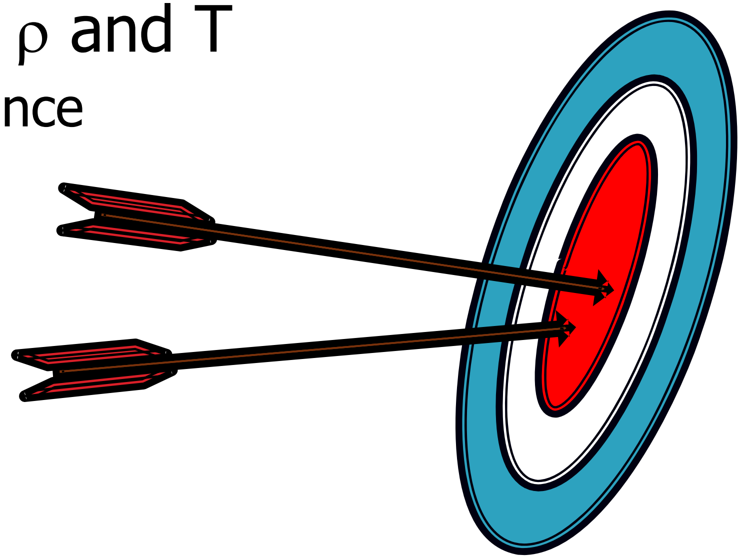
$$S \qquad P$$

$$\frac{C_v}{T} \longleftrightarrow \Gamma \longleftrightarrow \frac{\partial S}{\partial V} = \frac{\partial P}{\partial T} \longleftrightarrow \Pi \longleftrightarrow \frac{\partial P}{\partial V}$$

$$\frac{\partial^2 S}{\partial T^2} \qquad \frac{\partial^2 S}{\partial T \partial V} = \frac{\partial^2 P}{\partial T^2} \qquad \frac{\partial^2 S}{\partial V^2} = \frac{\partial^2 P}{\partial T \partial V} \qquad \frac{\partial^2 P}{\partial V^2}$$

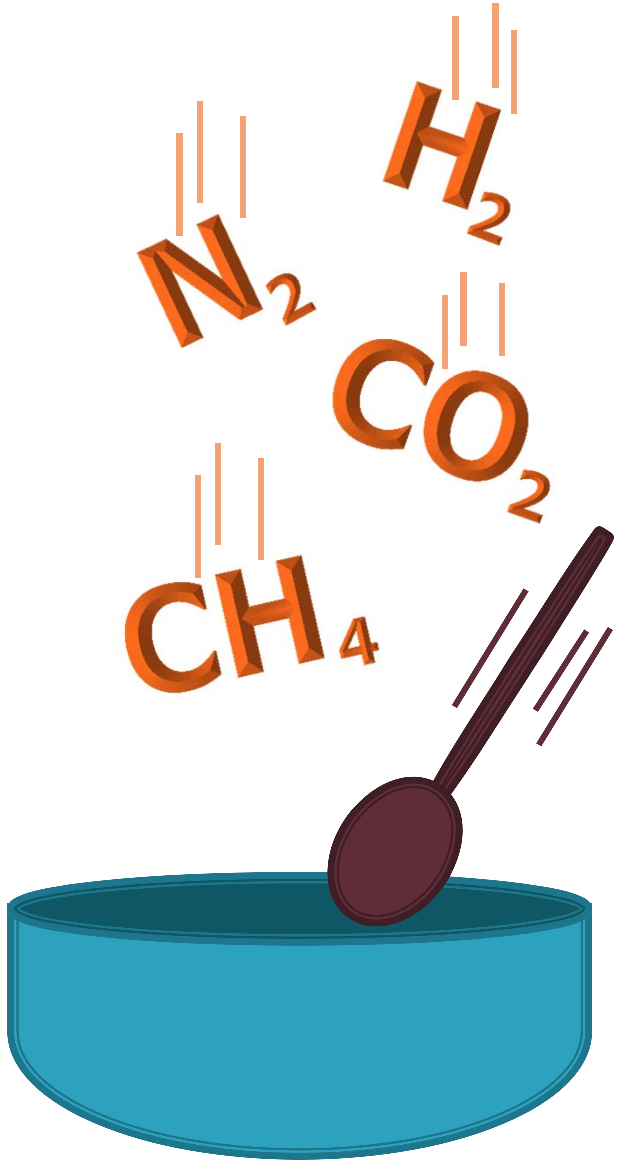
Mixture Equations of State

- Virial expansion
  - Gas phase only
- Extended corresponding states
  - Slow and sometimes nonconvergent
  - Has the ability for high accuracy
- Coefficient mixing of multiparameter equations
  - Requires fixed functional form for pure fluids
- Excess Helmholtz energy with ρ and T
  - High accuracy with high convergence

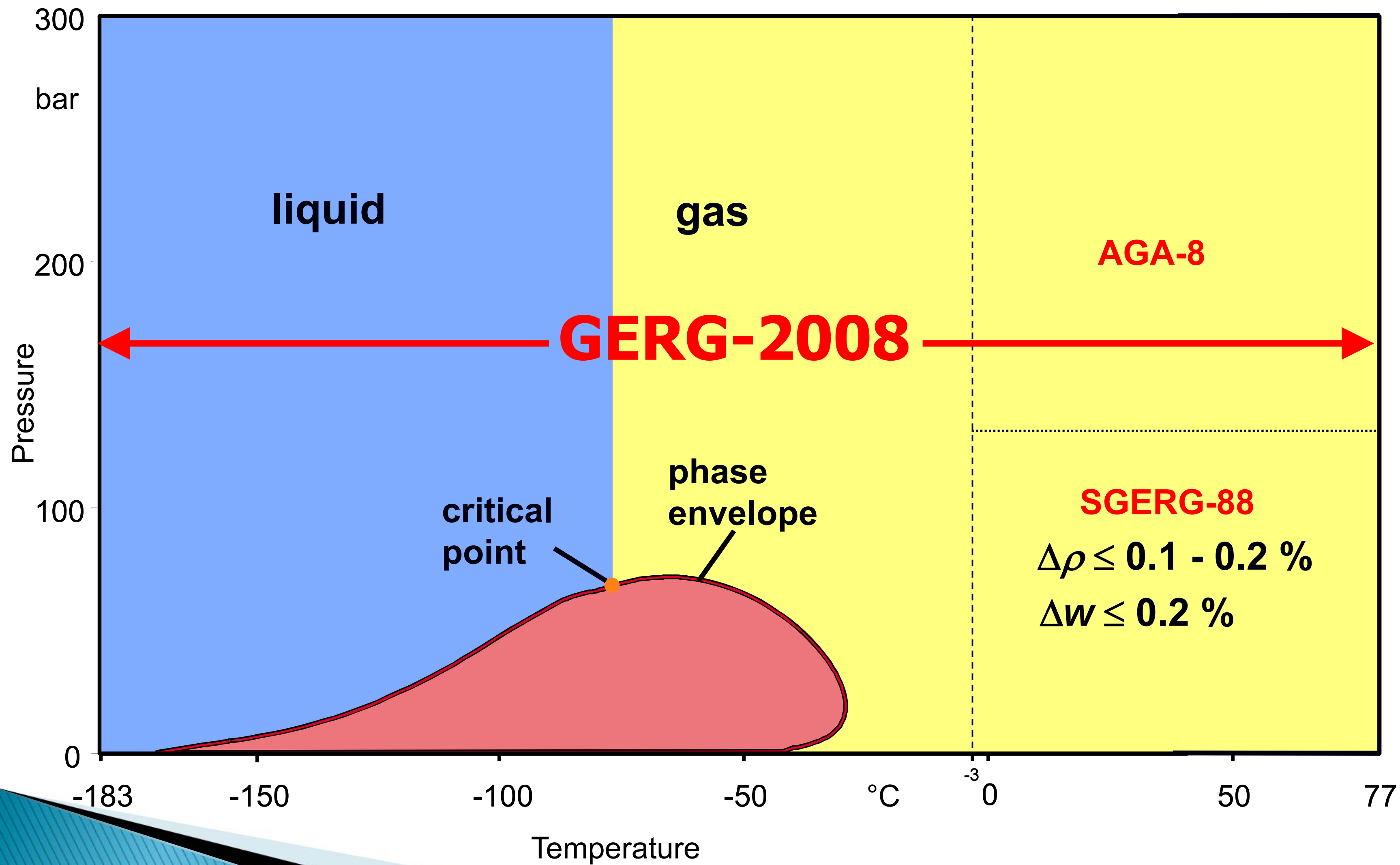


Mixture Equations of State

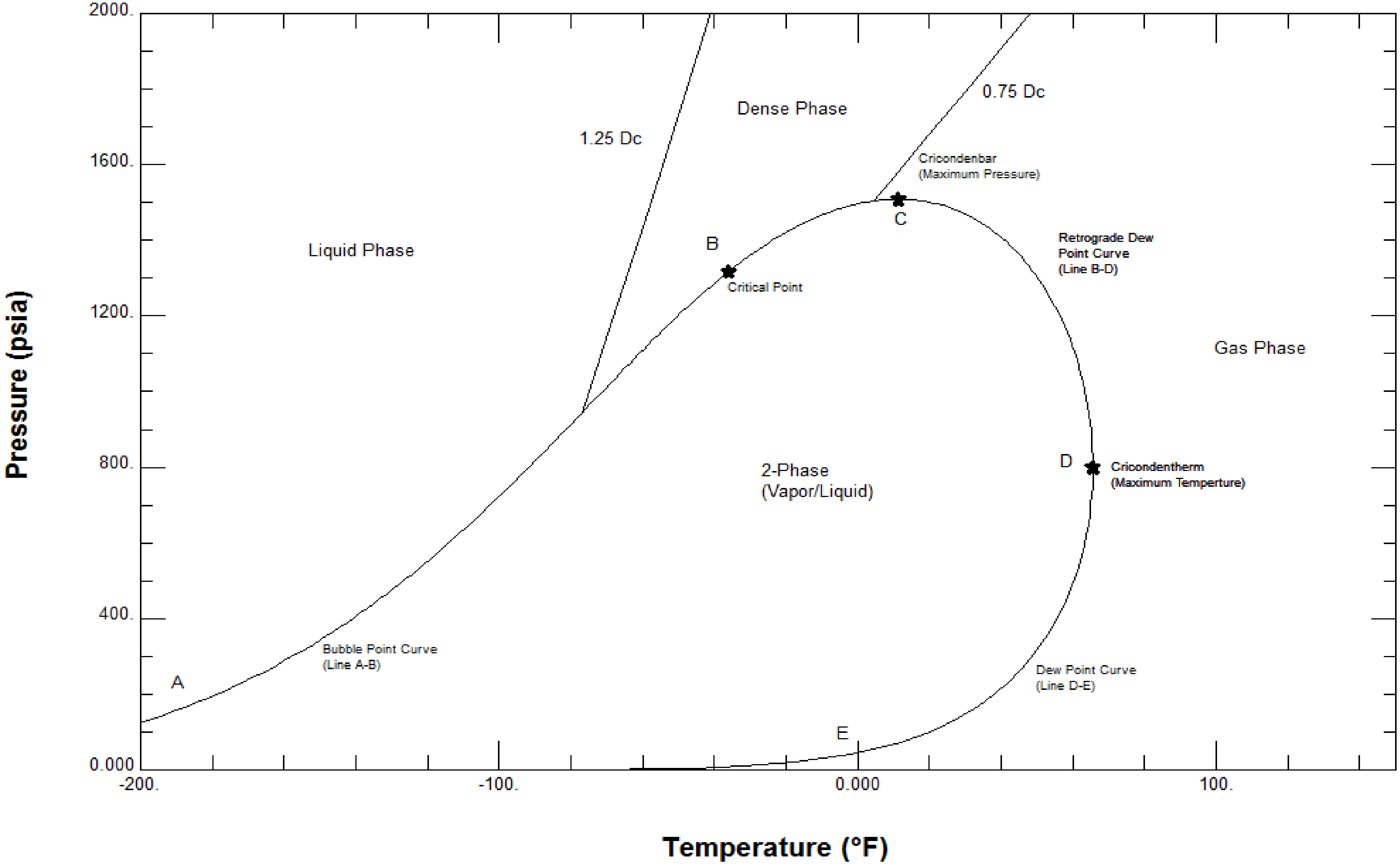
- Natural gas equations of state
  - SGERG-88 and AGA-8:
    - Volumetric properties only
    - Gas phase only
    - No dew points
- New reference equation of state
  - GERG-2008:
    - Volumetric and caloric properties
    - Fundamental equation of state
    - Valid for all fluid or gas states
    - Bubble and dew point calculations



Ranges of Application



Single-phase Boundary Definitions



GERG-2008 Helmholtz Energy EOS

$\delta = \rho / \rho_{\mathrm{r}}(\mathbf{x}) \quad \tau = T_{\mathrm{r}}(\mathbf{x}) / T$ **Reduced independent variables**

$$\alpha = \sum_{i=1}^{N} x_i \alpha_i^{\mathrm{ideal}}(\tau, \delta)$$ **Ideal gas contribution**

$$+ \sum_{i=1}^{N} x_i \alpha_i^{\mathrm{r}}(\tau, \delta)$$ **Pure fluid residual contribution**

$$+ \Delta\alpha(\tau, \delta, \mathbf{x})$$ **Excess mixture contribution**

GERG-2008 Reducing Functions

- Temperature and volume (density) reducing functions:

$$T_{\mathrm{r}}(\mathbf{x}) = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \beta_{T,ij} k_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} \left(T_{\mathrm{c},i} T_{\mathrm{c},j}\right)^{1/2}$$

$$v_{\mathrm{r}}(\mathbf{x}) = \frac{1}{8}\sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \beta_{v,ij} k_{v,ij} \frac{x_i + x_j}{\beta_{v,ij}^2 x_i + x_j} \left(v_{\mathrm{c},i}^{1/3} + v_{\mathrm{c},j}^{1/3}\right)^3$$

- Four parameters are available for fitting binary mixture data: β_T, k_T, β_V, and k_v

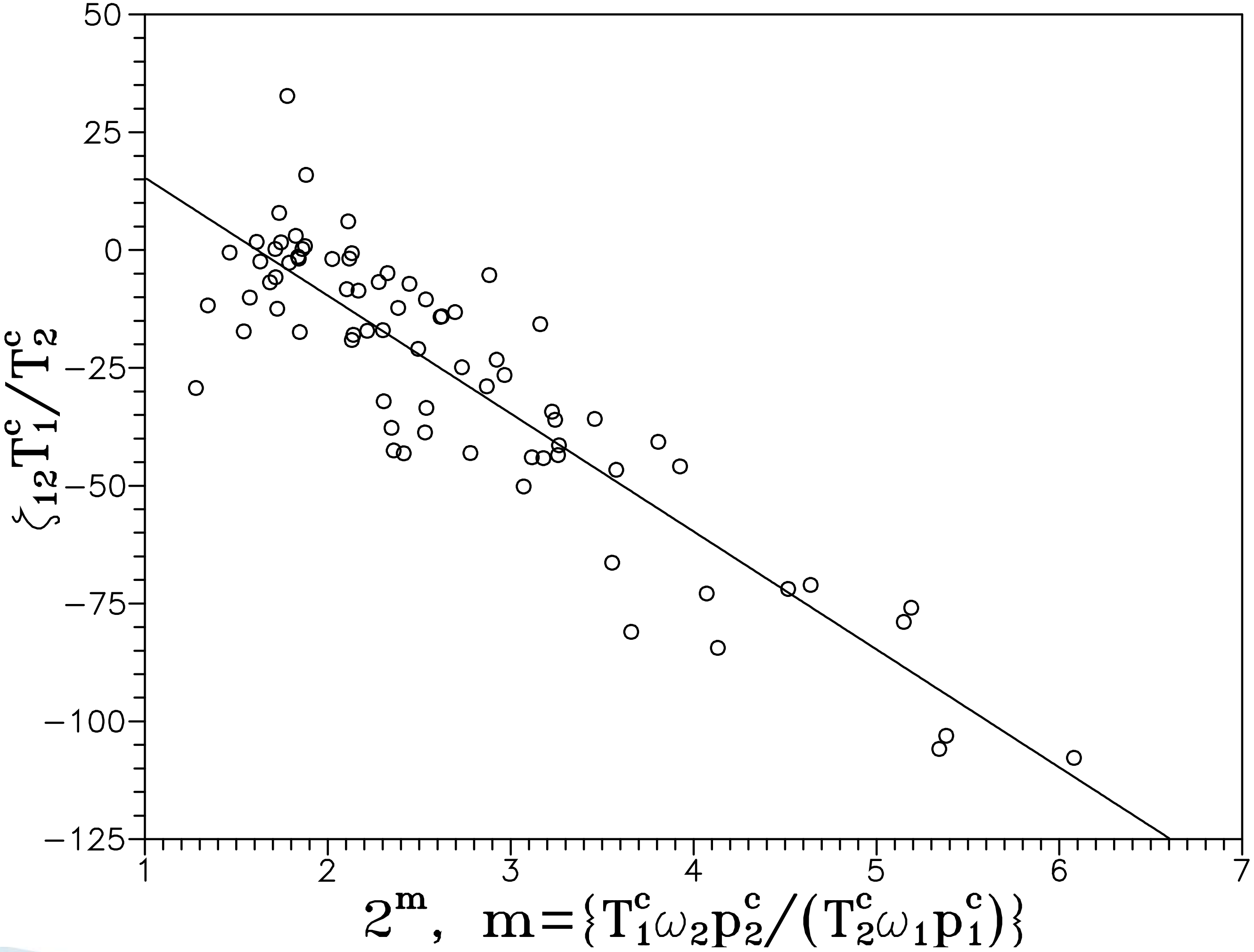
Prediction Scheme

- When data are not available to fit interaction parameters, estimation schemes can be used.
  - Critical temperatures, critical pressures, and acentric factors can be used to calculate the interaction parameter for the temperature reducing line:

$$\zeta_{pq} \frac{T_1^{\text{crit}}}{T_2^{\text{crit}}} = 40.4 - 25.03 \times 2^m$$

$$m = \left[\frac{T_1^{\text{crit}}}{T_2^{\text{crit}}} \frac{P_2^{\text{crit}}}{P_1^{\text{crit}}} \frac{\omega_2}{\omega_1} \right]$$

Comparisons of Fitted and Predicted Values



Richard Jacobsen

Ph.D. (original mBWR equation)	Nitrogen	1973
Jahangiri	Ethylene	1986
Jahangiri	Nitrogen	1986
Katti	Neon	1986
Lemmon	R11	1992
Penoncello	R12	1992
Kamei	R22	1995
Penoncello	Cyclohexane	1995
Lemmon	Air	2000
Leachman	Hydrogen	2009
Lemmon	Natural gas and refrigerant mixtures	1996

Wolfgang Wagner

- Schmidt Oxygen 1985
- Marx R11, R12 1992
  R22, R113
- Span CO_2 1996
- Tegeler Argon 1999
- Span Nitrogen 2000
- Smukala Ethylene 2000
- Setzmann Methane 2000
- Pruss Water 2002
- Ethane Buecker 2006
- Butanes Buecker 2006
- Guder SF6 2009
- Kunz GERG-2008

Roland Span

- Chair of mechanical engineering in Bochum.
- Developed equations of state for:

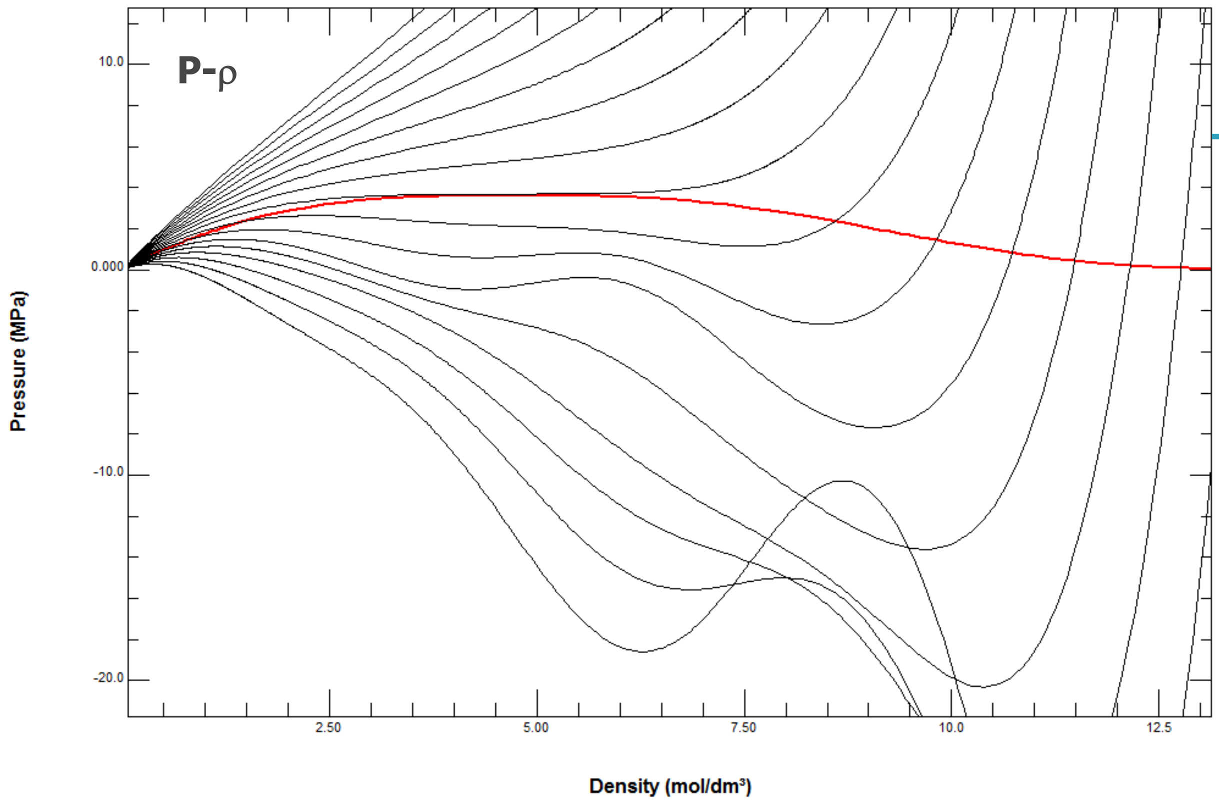
Ammonia	Oxygen
Argon	Pentane
Butane	Propane
CO_2	R-11
Cyclohexane	R-113
Ethane	R-12
Ethylene	R-123
Heptane	R-125
Heptane	R-134a
Hexane	R-143a
Isobutane	R-152a
Methane	R-22
Nitrogen	R-32
Octane	SF6

- Developed a generalized correlation requiring only the critical point and acentric factor.
- Has too many students to count.

Me

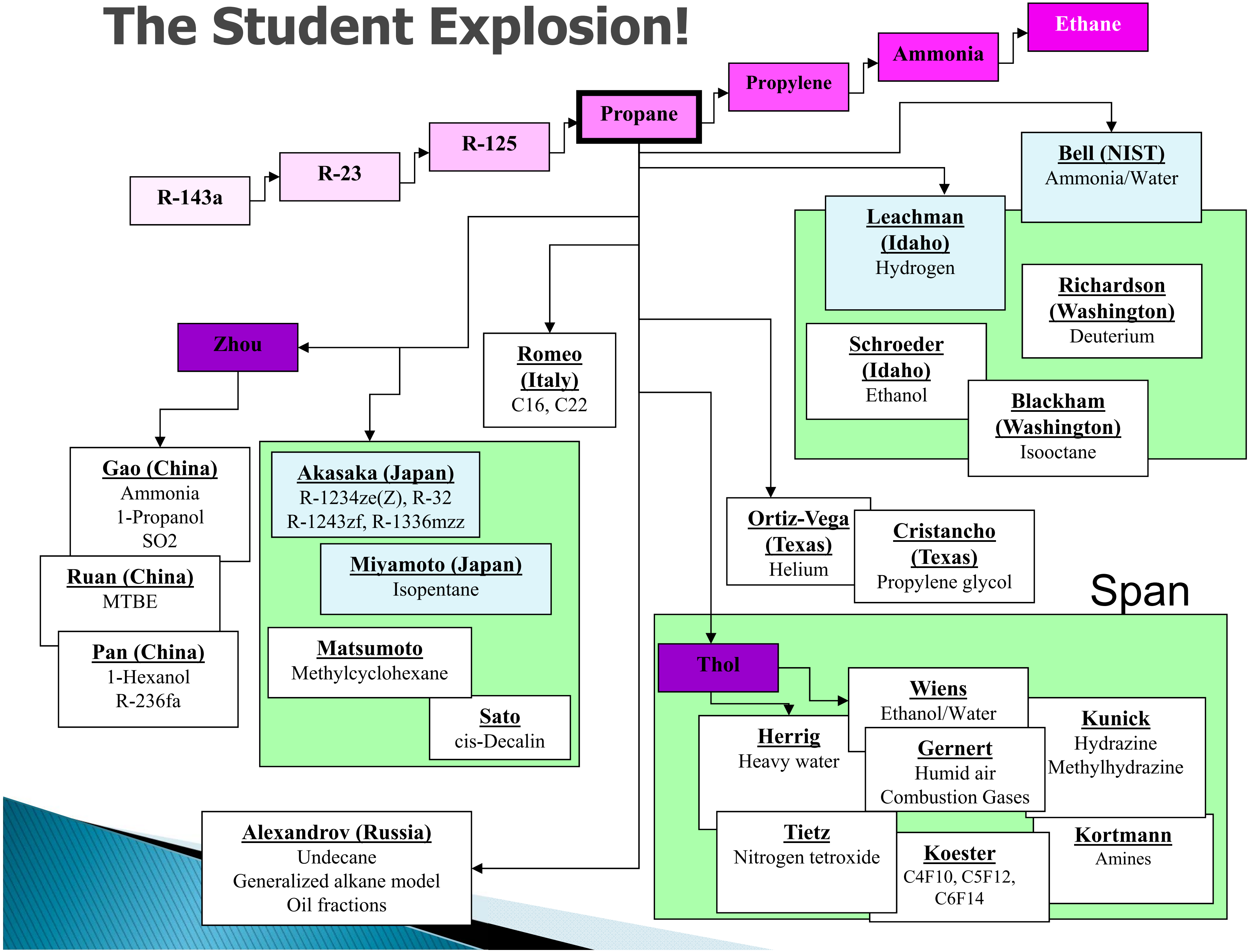
- Developed equations of state for:
  - Air
  - Acetone
  - Butene
  - Carbon monoxide
  - Carbonyl sulfide
  - Cis-butene
  - Cyclopentane
  - Decane
  - Dodecane
  - Hydrogen sulfide
  - Isobutene
  - Isohexane
  - Isopentane
  - Krypton
  - Methyl linoleate
  - Methyl linolenate
  - Methyl oleate
  - Methyl palmitate
  - Methyl stearate
  - Methylcyclohexane
  - Neopentane
  - Nitrous oxide
  - Nonane
  - Propylcyclohexane
  - R-11
  - R-115
  - R-116
  - R-1233zd(E)
  - R-1234yf
  - R-141b
  - R-142b
  - R-218
  - R-227ea
  - R-365mfc
  - R-41
  - Sulfur dioxide
  - Toluene
  - Trans-butene
  - Trifluoroiodomethane
  - Xenon
- Mixture models for natural gas, refrigerants, and cryogens.
- Refprop

Nonlinear Fitting Timeline

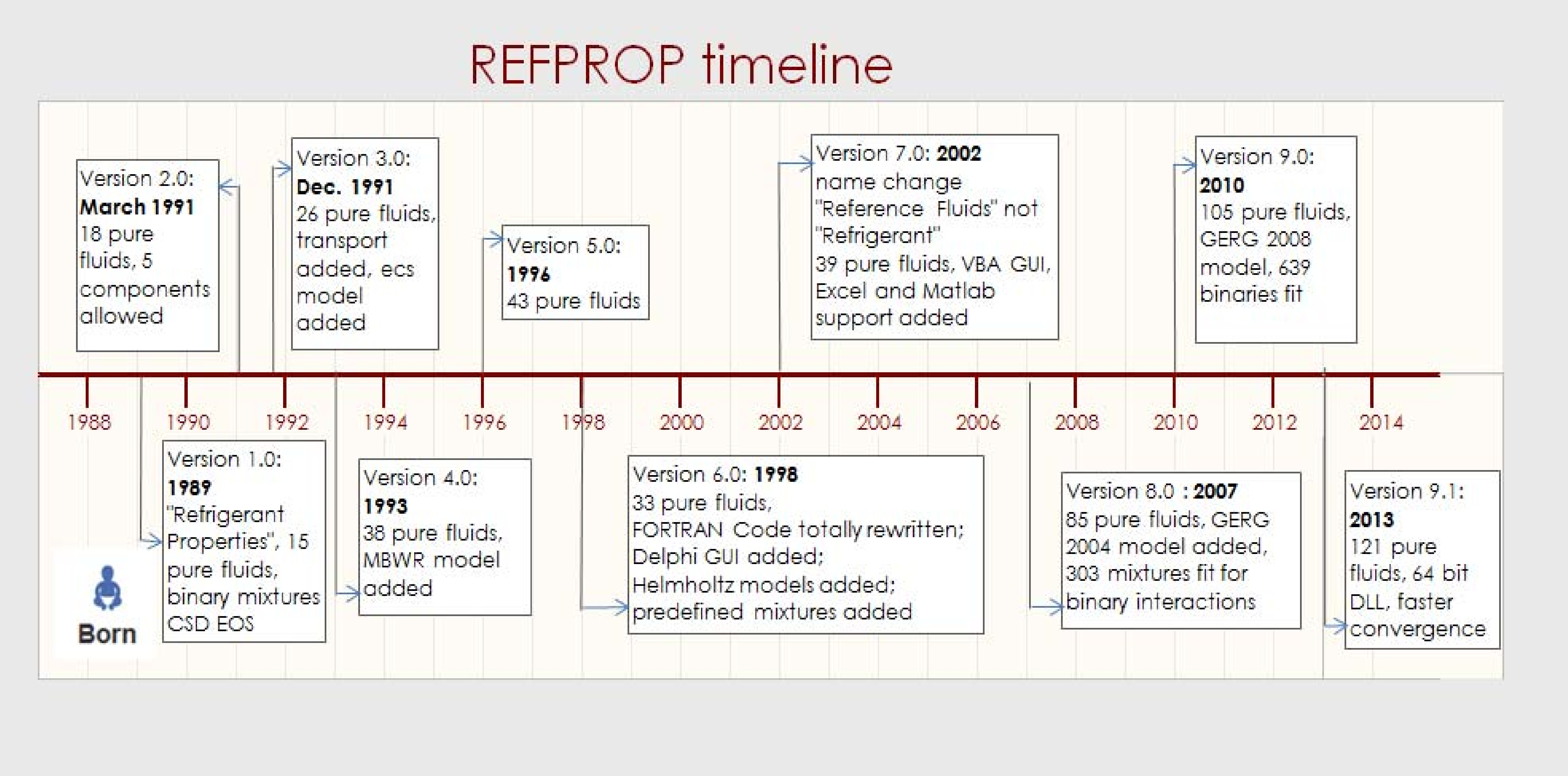


- R-143a 1999
- R-23 2000
- R-125 2002
- Propane 2007
- Propylene 2010
- Ammonia 2016
- Ethane 2020?

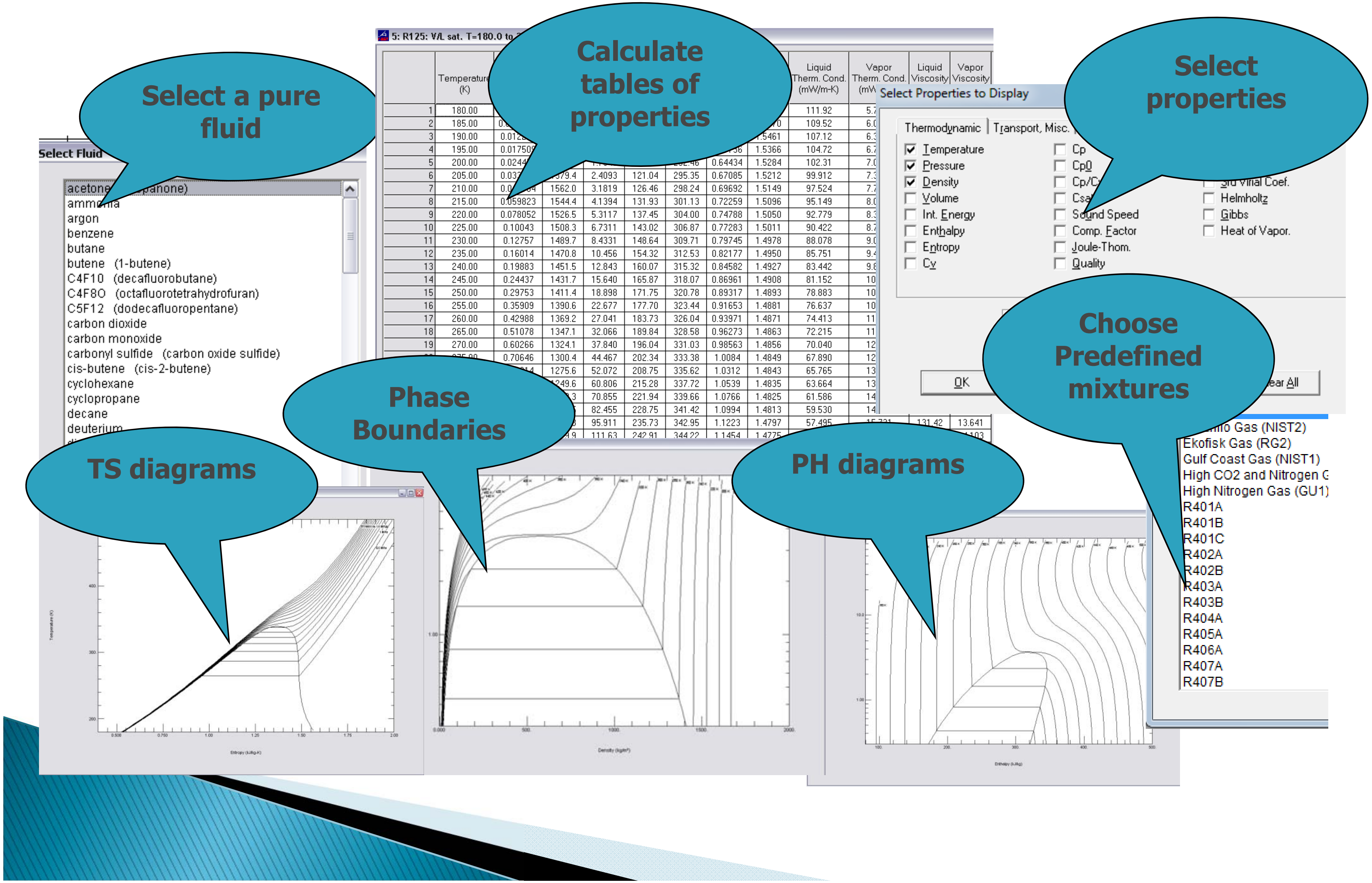
The Student Explosion!



REFPROP - History

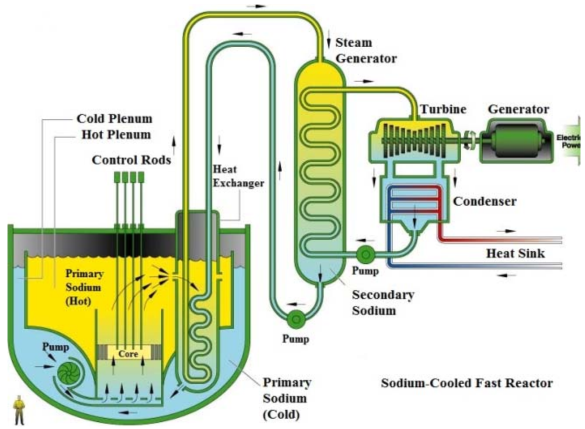


REFPROP – What does it look like?

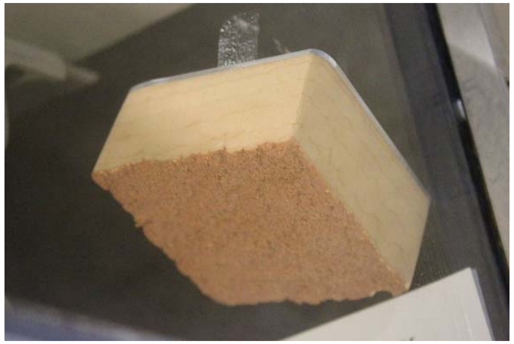


REFPROP – Is It Actually Used?

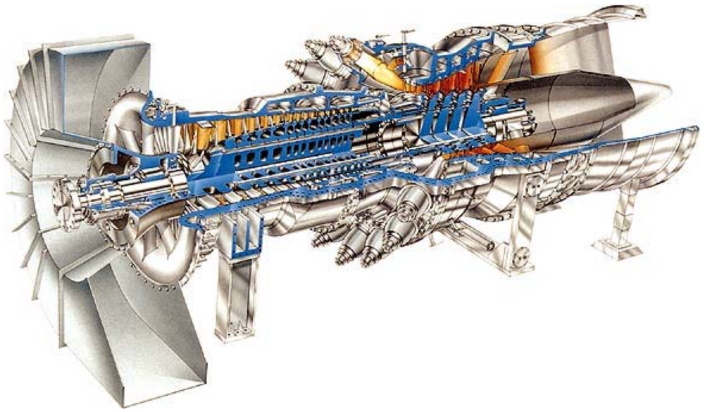
- Nuclear Engineering
  - Recently cited by Jeong et al. in Nuclear Engineering and Design where REFPROP was used for CO2 properties to design a sodium fast-cooled reactor with a supercritical CO2 Brayton cycle.
- Design of working fluids for solar organic Rankine cycles
  - Rayegan and Tao in Renewable Energy used REFPROP to explore efficiency with different fluids.
- Modeling the volatiles in volcanic eruptions
  - Researchers at the University of Vancouver used REFPROP to model the volatiles of a volcanic eruption as a mixture of CO2 and water.



REFPROP – Is It Actually Used?

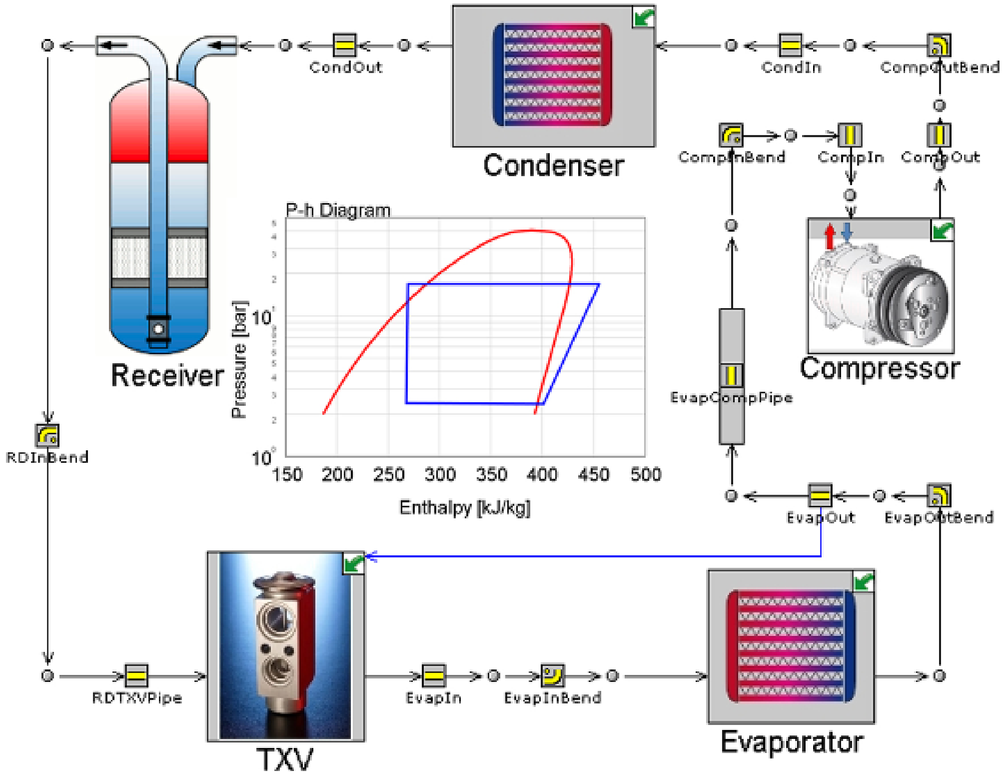


- NASA
  - Nitrogen calculations to investigate the cause of the Columbia space craft accident.
  - Europa clipper mission.
  - Cryogenic systems for Mars missions.
- SpaceX
  - Fuels (for example, methane and liquid oxygen) and system components design.
- Aircraft and turbine design
- CERN
  - Attaining cryogenic conditions of the magnets.



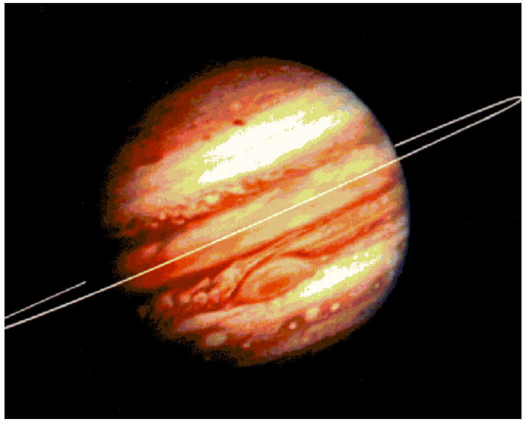
REFPROP – Is It Actually Used?

- Automotive Industry
  - Everything from combustion to refrigerant and fuels.
  - The picture below shows an example from an industrial program of a complex automotive refrigerant design, with a REFPROP diagram in the middle.

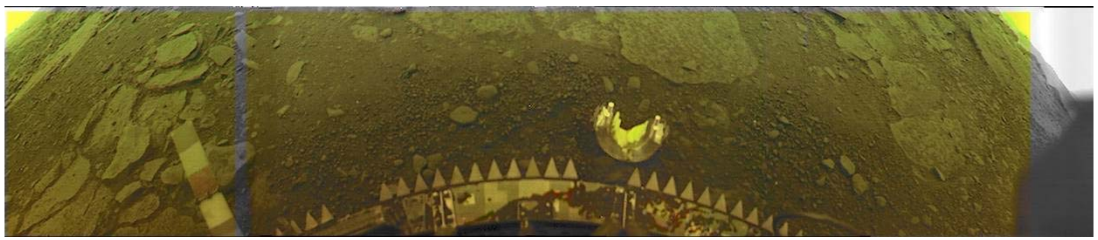


REFPROP – Is It Actually Used?

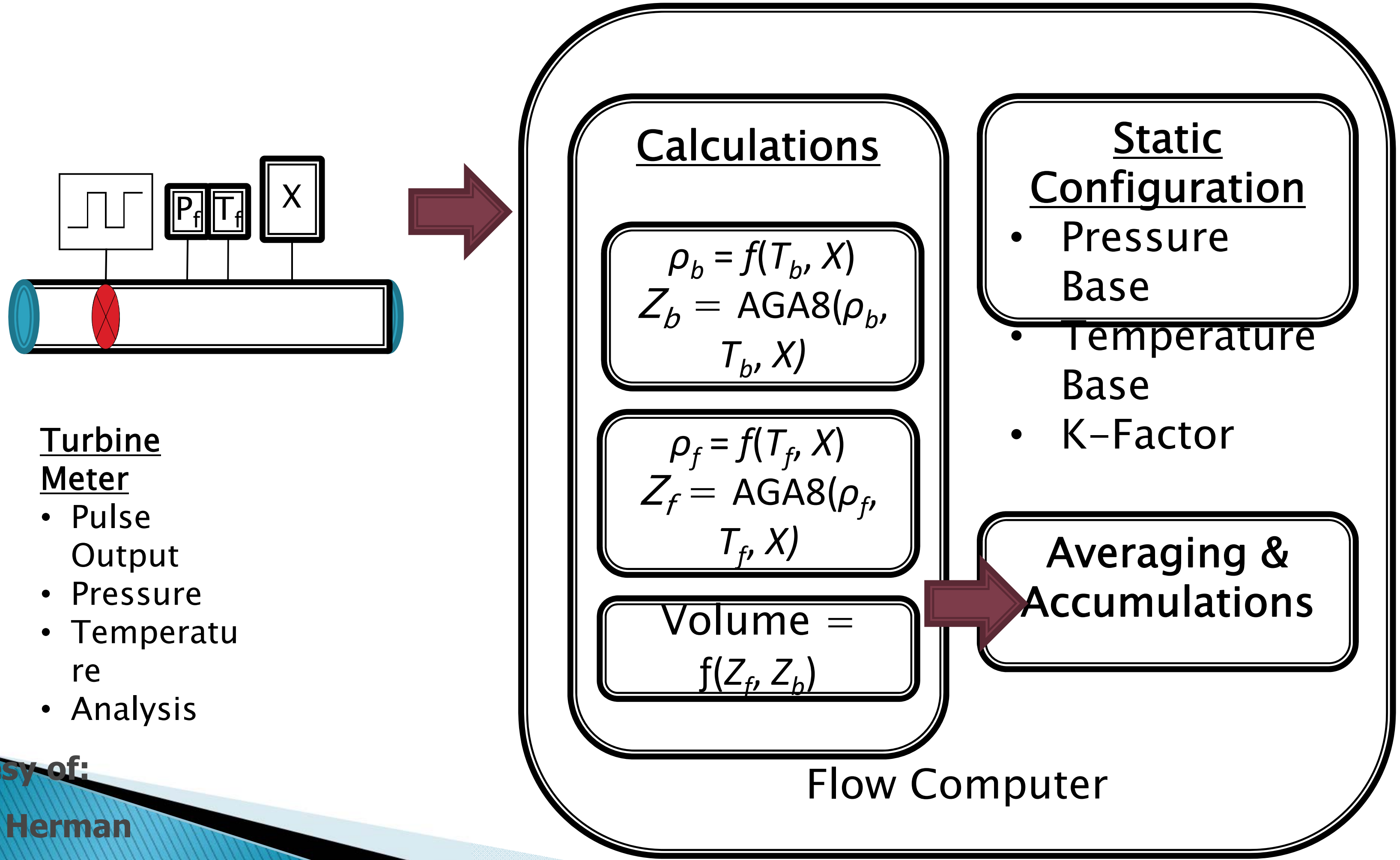
- Some out-of-this-world examples
- Modeling the atmosphere on Jupiter
  - 86% hydrogen / 14% helium used to model the Jovian atmosphere in a project to design a nuclear ramjet for use on the surface of Jupiter.
- Image processing of the surface of Venus
  - To provide properties of the atmosphere on Venus.
- To aid in the search for dark matter.
  - Researchers at the University of Chicago searching for WIMP (weakly interacting massive particles) dark matter with CF3I bubble chambers.



Actual image taken by probe on surface of Venus



Simplified Data Flow



Courtesy of:
Randy Herman
Flow Cal, Houston