Cubic Virial Equation of State

Silicon Valley FIG

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Chen-Hanson Ting

Equations of State

Functional relationship among pressure, volume and temperature of gases:

Boyle's Law (1662)

$$PV = \text{constant}$$

Charles's Law (1787)

$$V = \text{constant} * T$$

The Ideal Gas Law (1834)

$$PV = nRT$$

Equations of State

Real gases deviate from the Ideal Gas Law:

Van der Waals EOS (1873)
$P = RT/(V-b) + a/V^2$

Dieterici EOS (1899)
$P = (RT/(V-b))\exp(-a/RTV)$

Berthelot EOS (1907)
$P = RT/(v-b) - a/TV^2$

Equations of State

Most other EOS are variants of van der Waals EOS

Redlich-Kwong EOS (1949)

$$P = RT/(V-b) - a/(T^{1/2}V(V+b))$$

Soave-Redlich-Kwong EOS (1972)

$$P = RT/(V-b) - a\alpha/(V(V+b))$$

Peng-Robinson EOS (1976)

$$P = RT/(V-b) - a\alpha/(V(V+b) - V(V-b))$$

Equations of State

Other EOS are based on Virial Expansion:

Kamerlingh Onnes EOS (1901)

$$P=(RT/V)(1+B/V+C/V^2+D/V^4+E/V^6+F/V^8)$$

Beattie-Bridgeman EOS (1927)

$$P=RT(1-c/T^3V)(V+B_0(1-b/V))/V^2 \\ -A_0(1-a/V)/V^2$$

Benedict-Webb-Rubin EOS (1940)

$$P=RT/V+B/V^2+C/V^3+D/V^6 \\ +(E/V^3)(1+F/V^2)\exp(-F/V^2)$$

Equations of State

Van der Waals EOS has a singular point at V=b. It does not allow investigation into the region V<b.

Non van der Waals EOS are generally complicated beyond comprehension.

Cubic Virial Equation

A virial EOS truncated to the third term

$$P = RT/V - B/V^2 + C/V^3$$

It has all the nice properties of van der Waals EOS, but without the singular point.

Cubic Virial Equation

At the critical point, $dP/dV=0$ and $d^2P/dV^2=0$ lead to

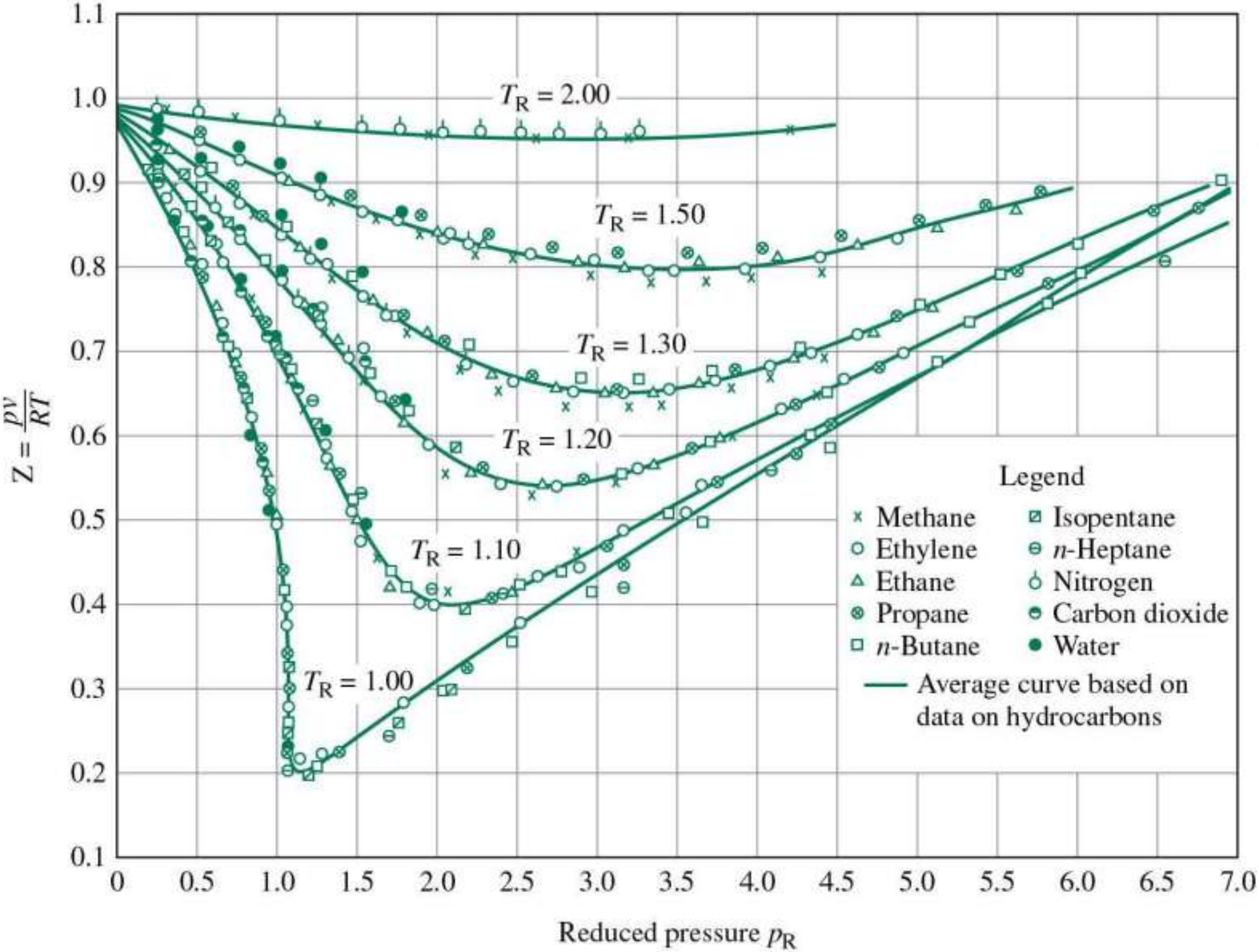
$$B = V_C,\quad C = V_C^2/3$$

A reduce EOS becomes

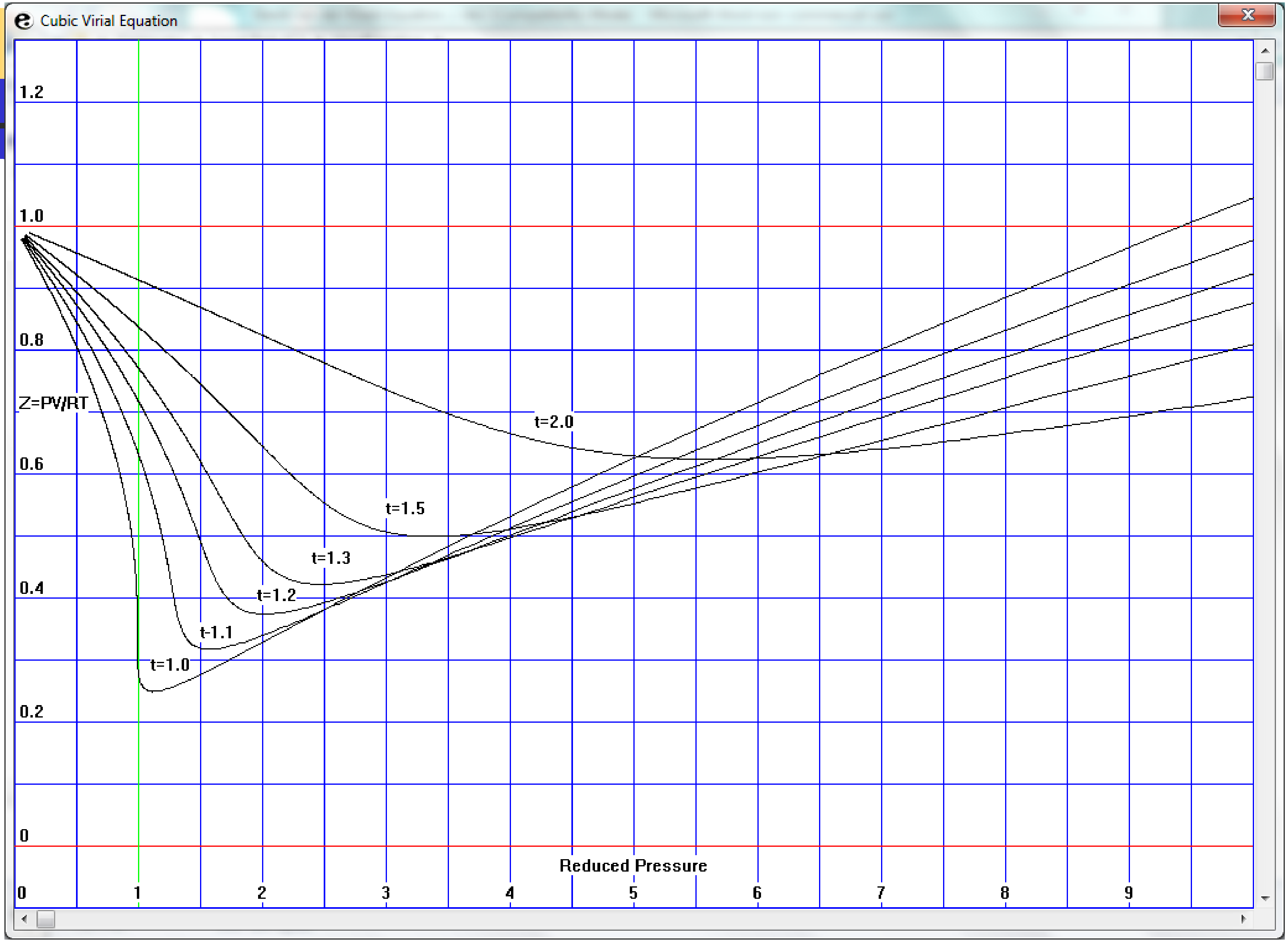
$$p = 3t/v - 3/v^2 + 1/v^3$$

$$(\,p=P/P_C \quad v=V/V_C \quad t=T/T_C\,)$$

Z-Plots of Real Gases



Z-Plots of Cubic Virial EOS



Scaled Cubic Virial EOS

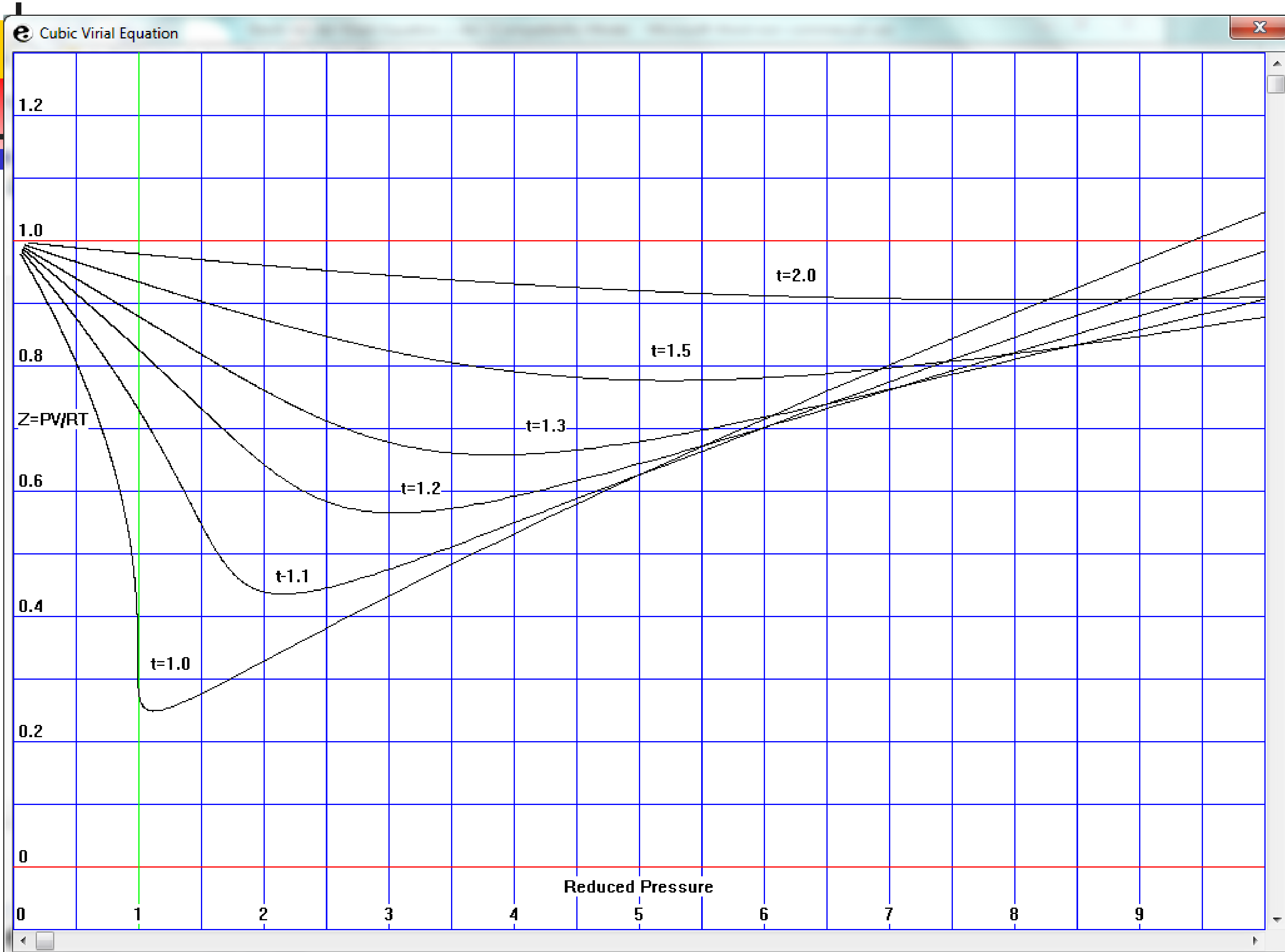
The Z-plots are too low for reduced temperatures t>1.

A reduce EOS must be scaled by $1/t^2$

$$p = 3t/v - (3/v^2 + 1/v^3)/t^2$$

The Z-plots are brought to within 5% of experimental Z values.

Scaled Cubic Virial EOS



Gas-Liquid Equilibrium

Under saturation pressure, Gibbs free energy of gas must equal to that of liquid. Under constant temperature, Gibbs free energy can be computed from a PVT isotherm:

$$G = \int v\,dp = pv - \int p\,dv$$

Gibbs free energy curve crosses itself at the saturation pressure.

Gas-Liquid Equilibrium

Between critical point and triple point, EOS(7) needs to be scaled by $t^{1/2}$(12) or t(13) to determine the saturation pressure:

$$p = 3t/v - 3/v^2 + 1/v^3 \qquad (7)$$
$$p = 3t/v - 3/t^{1/2}v^2 + 1/t^{1/2}v^3 \qquad (12)$$
$$p = 3t/v - 3/tv^2 + 1/tv^3 \qquad (13)$$

Gas-Liquid Equilibrium

Reduced T	Reduced Saturation Pressure			
	Exper.	**Eq. 7**	**Eq. 12**	**Eq.13**
0.9	0.538	0.69	0.62	0.55
0.8	0.256	0.47	0.35	0.26
0.7	0.100	0.30	0.17	0.095
0.6	0.028	0.16	0.055	Note a
0.5	Note b	0.10	Note a	Note a

Gas-Liquid Equilibrium

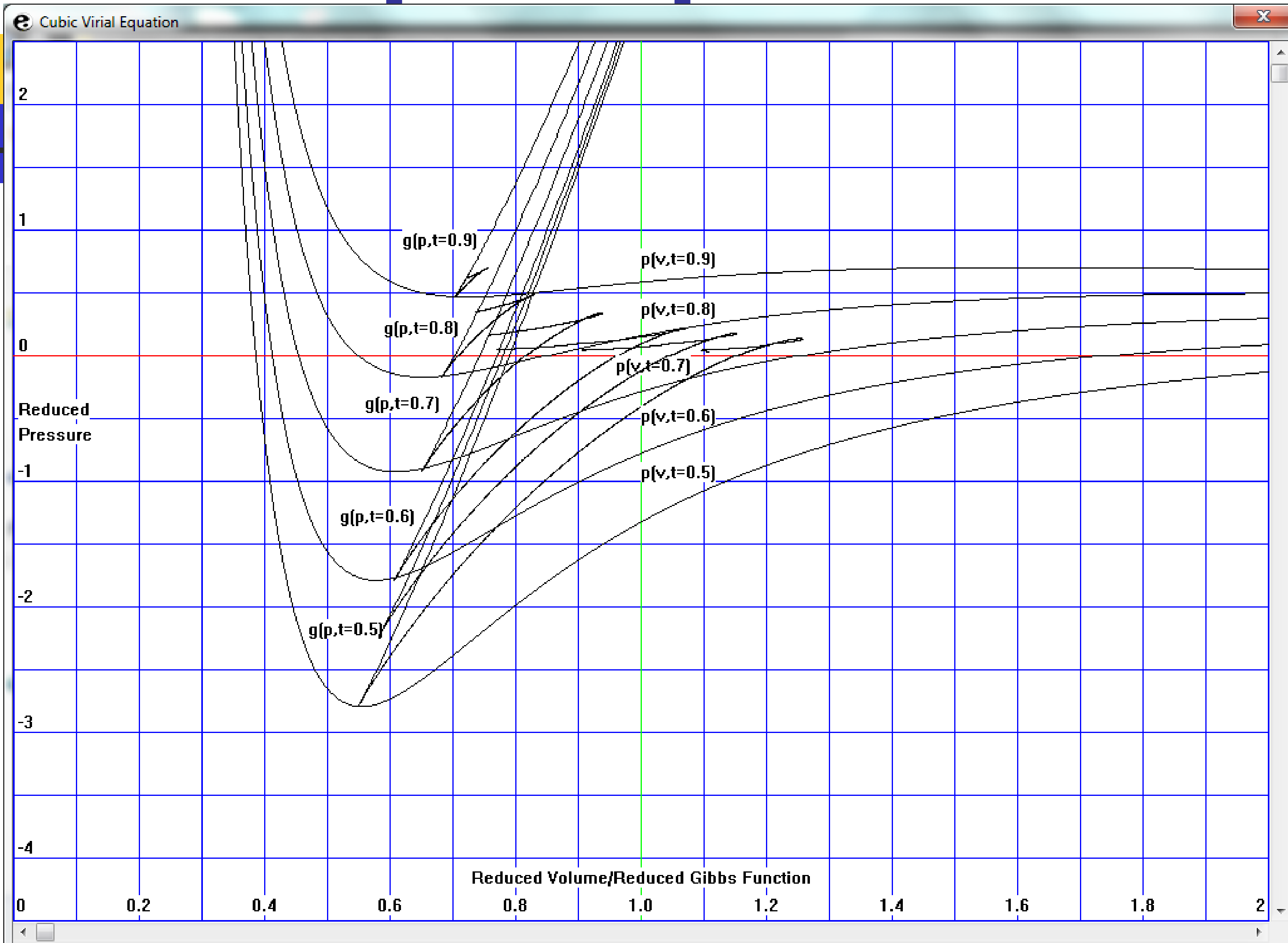
It looks like the best solution is between Eq. 12 and Eq. 13, a bit closer to Eq. 12.

$$p = 3t/v - 3/v^2 + 1/v^3 \qquad (7)$$

$$p = 3t/v - 3/t^{1/2}v^2 + 1/t^{1/2}v^3 \qquad (12)$$

$$p = 3t/v - 3/tv^2 + 1/tv^3 \qquad (13)$$

Gas-Liquid Equilibrium



Gas-Liquid-Solid Phases

Cubic virial EOS

$p = 3t/v - 3/v^2 + 1/v^3$ (7)

First term $3t/v$ is kinetic energy

Second term $-3/v^2$ is attraction between two molecules

Third term $1/v^3$ is repulsion among molecules in close contact

Gas-Liquid-Solid Phases

Cubic virial EOS

$$p = 3t/v - 3/v^2 + 1/v^3 \qquad (7)$$

There are three roots for this equation when $t<1$. These roots account for the equilibrium between gaseous and liquid phases.

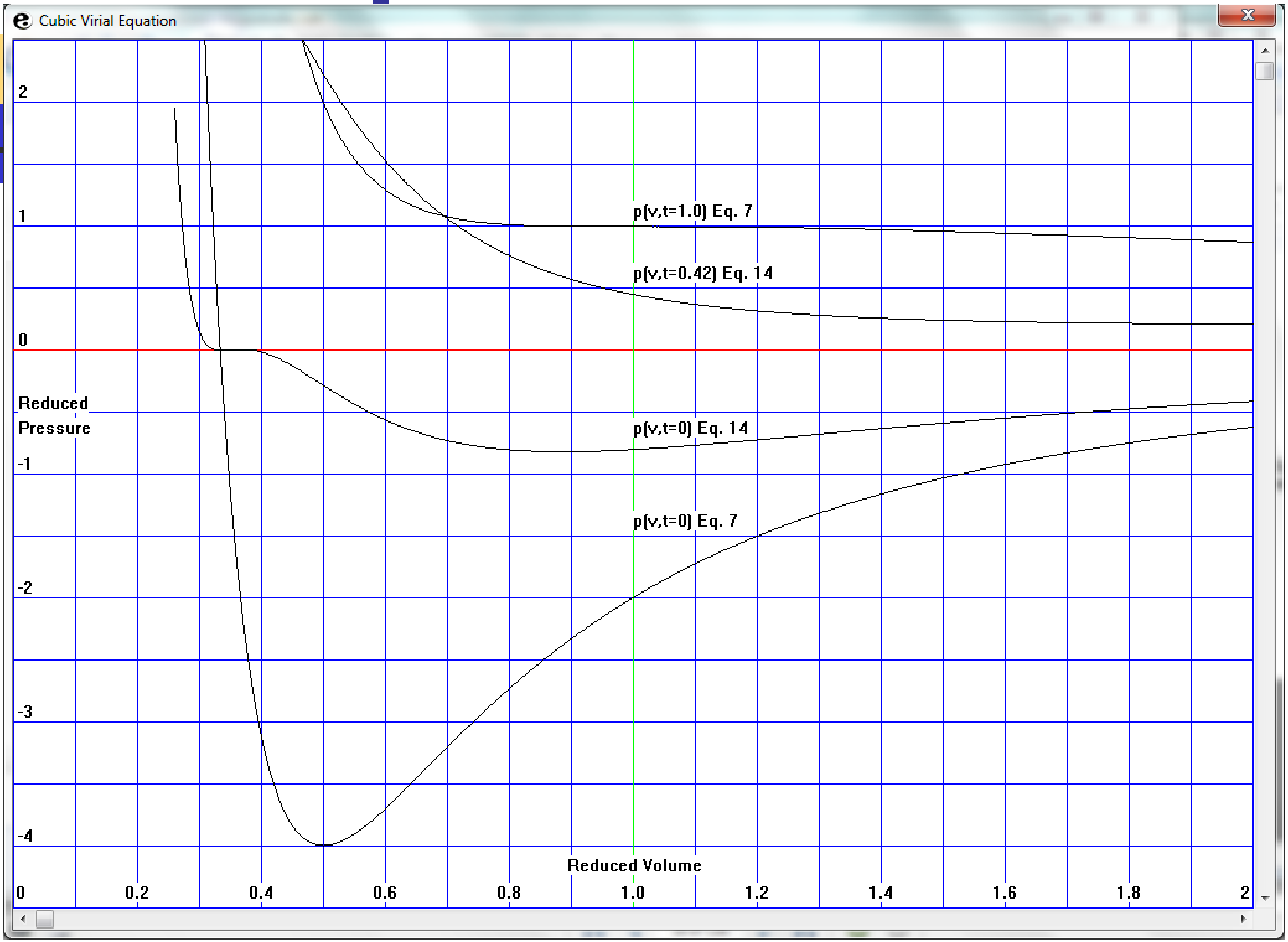
Gas-Liquid-Solid Phases

A fifth order virial EOS in the form of:
$$p = 3t/v - 3(1-v_s/v)(1-v_m/v)(1-v_l/v)/v^2$$

It could have 5 roots, and give rise of a solid phase.

If $t=0$, there might be 3 roots at v_s for a solid phase, v_l for a liquid phase, and a intermediate root at v_m.

Gas-Liquid-Solid Phases



Gas-Liquid-Solid Phases

A fifth order virial EOS in the form of:
$p = 3t/v - 3(1-v_s/v)(1-v_m/v)(1-v_l/v)/v^2$

This EOS does not work. Three roots are too shallow for a solid phase which is stable over a wide temperature range. The critical point is also shifted to a wrong place.

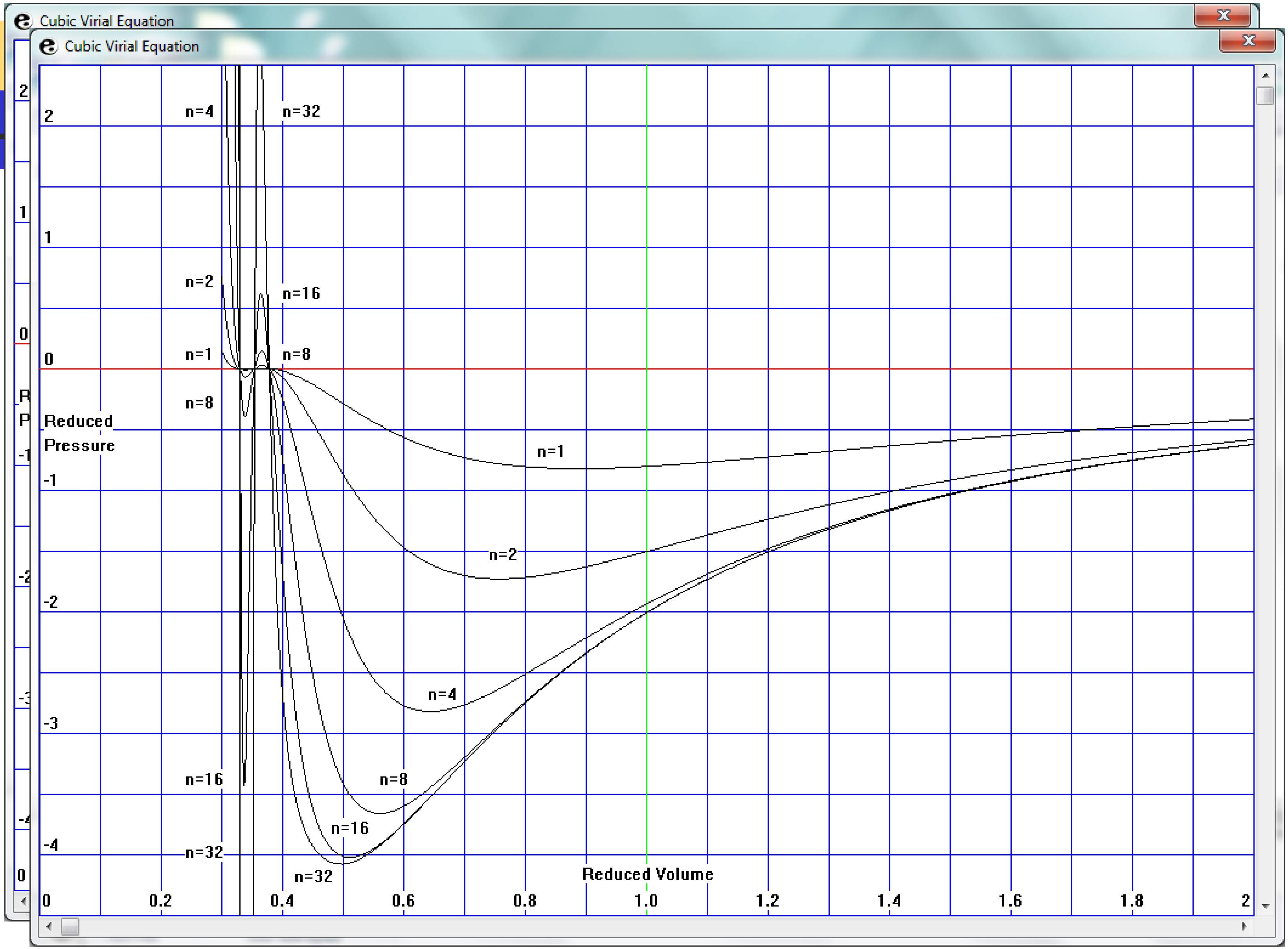
Gas-Liquid-Solid Phases

A very high order virial EOS is necessary:

$p = 3t/v - 3(1-v_s/v)(1-(v_m/v)^n)(1-(v_l/v)^n)/v^2$

This EOS still has three roots at v_s, v_l and v_m. The S-shaped bend between v_s and v_l can be make very sharp and very steep, by raising (v_m/v) and (v_l/v) to high powers. The power factor n will be determined graphically.

Gas-Liquid-Solid Phases



Gas-Liquid-Solid Phases

The best virial EOS is with n=26:

$p = 3t/v - 3(1- v_s/v)(1-(v_m/v)^{26})(1-(v_l/v)^{26})/v^2$

For Argon at the triple point,

$t=0.553$

$p=0.0142$

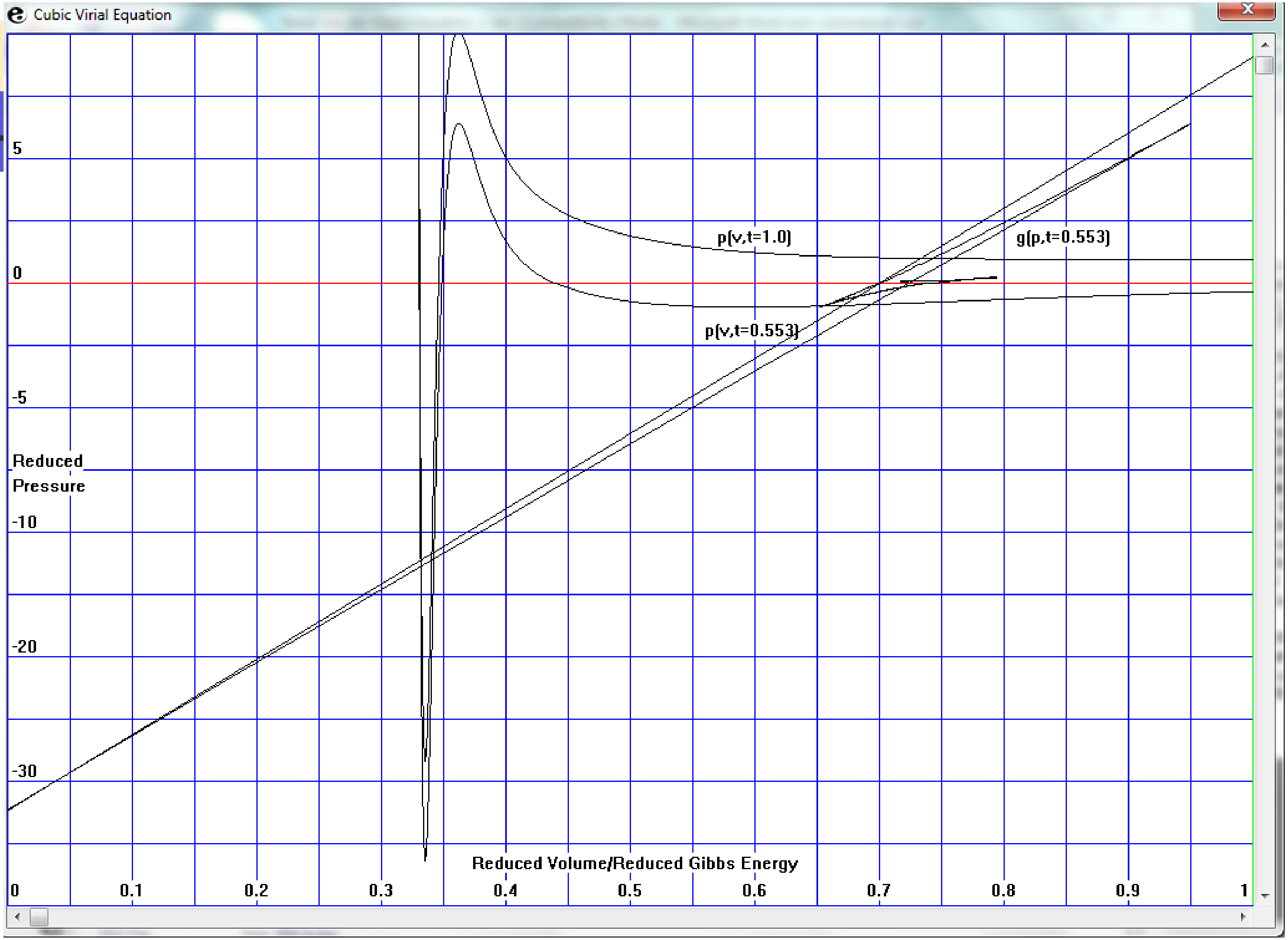
$v_s=0.330$

$v_l=0.378$

$v_m=0.354$

$n=26$

Gas-Liquid-Solid Phases



Gas-Liquid-Solid Phases

The best virial EOS is with n=26:

$p = 3t/v - 3(1- v_s/v)(1-(v_m/v)^{26})(1-(v_l/v)^{26})/v^2$

The Gibbs free energy curve at t=0.553 crosses itself at p=0, indicating that a solid phase is in equilibrium with a liquid phase. The pressure is low, and the gaseous phase behaves like ideal gas, coexisting with solid and liquid phases.

Conclusions

A cubic virial EOS has all the nice properties of van der Waals EOS without the problematic singular point.

The cubic virial EOS can be modified to

$p = 3t/v - 3(1- v_s/v)(1-(v_m/v)^{26})(1-(v_l/v)^{26})/v^2$

and it can account for the coexistence of gaseous, liquid and solid phases.

Questions?

Thank You Very Much!