Virial Expansion

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Virial Expansion

This paper was uploaded to Wikipedia.

Google 'virial expansion' and you will find it.

Let's first scan through it on Wiki.

Summary

- Second and Third Virial Coefficients
- Casting Equations of State into Virial Form
- Cubic Virial Equation of State
- Gas-Liquid-Solid Equilibrium
- State of Virial Equations

Gas-Liquid-Solid Equilibrium

Since 1972, I have struggled with the possibility of describing gas-liquid-solid equilibrium with an equation of state.

I picked up this problem again in 2015. After several try-and-error attempts, now I have a very simple virial equation of state doing exactly that.

Ideal Gas Law

The ideal gas law:
$Pv = RT$

It can be states in terms of compressibility:
$Z = Pv/RT = 1$

Virial Equation of State

Virial equation of state for real gases:
$Z=Pv/RT$
$=A+B/v+C/v^2+D/v^3+E/v^4+F/v^5+ \ldots$

A=1: real gases behave like ideal gas when v is large.

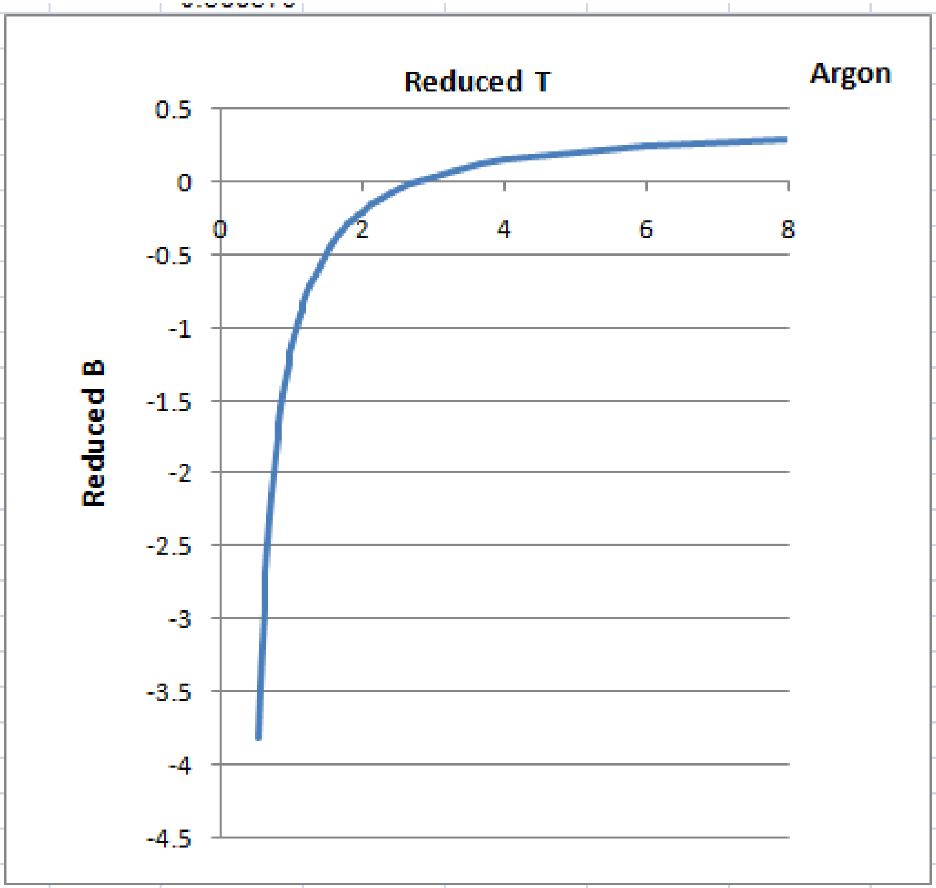
2^{nd} and 3^{rd} Virial Coefficents

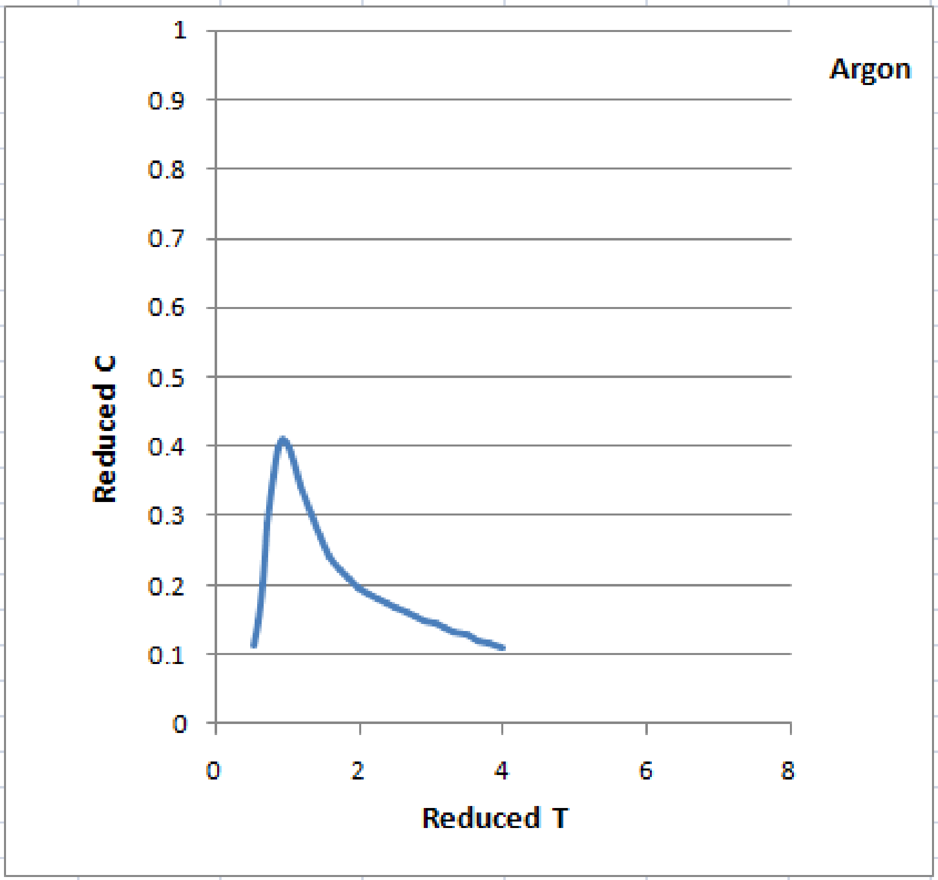
B: Second virial coefficient represents bimolecular attraction.

C: Third virial coefficient represents tri-molecular repulsion.

etc…

2nd and 3rd Virial Coefficients





3rd Virial Coefficent

My expectation is that the third virial coefficient must be a monotonically decreasing function of temperature. Otherwise, liquid could not coexist with gas below the critical temperature.

Accurate equations of state should confirm my expectation.

Some Equations of State

Van der Waals EOS (1873)

$P=RT/(V-b)+a/V^2$

Kamerlingh Onnes EOS (1901)

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

Benedict-Webb-Rubin EOS (1940)

Starling EOS (1972)

$P=RT/V+B/V^2+C/V^3+D/V^6$

$+(E/V^3)(1+F/V^2)\exp(-F/V^2)$

Cast EOS into Virial Forms

Van der Waals EOS

$P=RT/(V-b)+a/V^2$

Cast it into virial equation of state:

$P=(RT/V)(1+(b-a/RT)/V+b^2/V^2+b^3/V^3+\ldots)$

Third virial coefficient is a constant, and obviously not correct.

Cast EOS into Virial Forms

Benedict-Webb-Rubin EOS

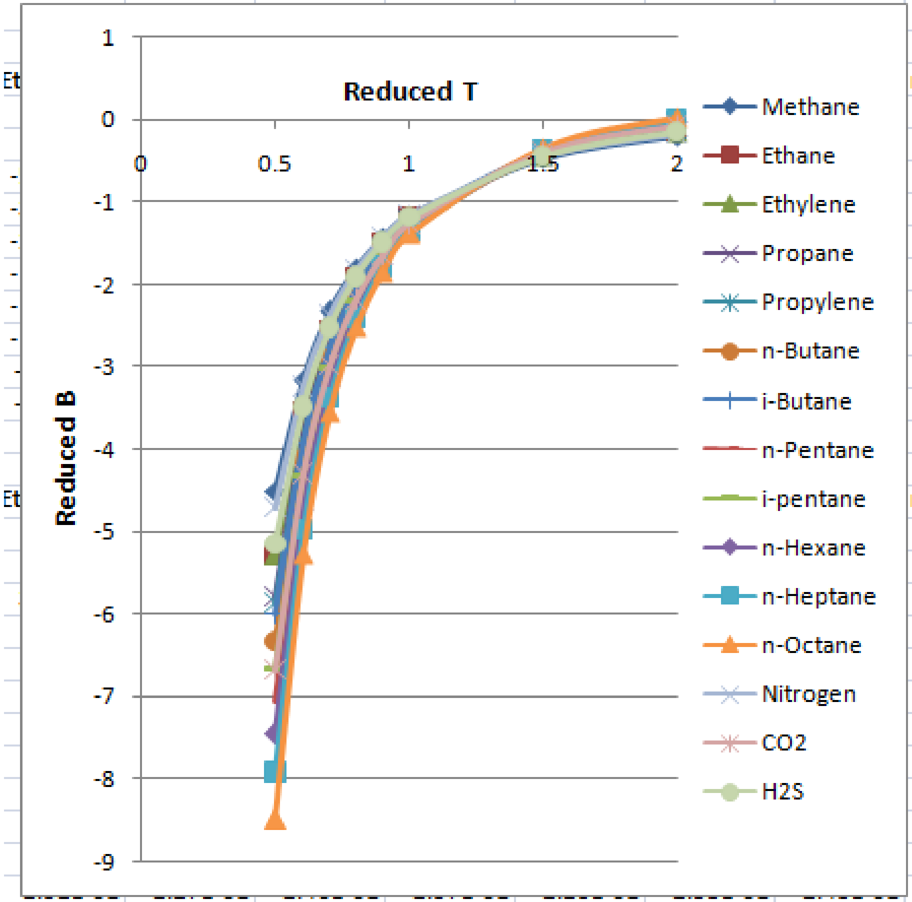
$P=RT/V(1+(B_0-A_0/RT-C_0/RT^3)/V+(b-a/RT)/V^2$
$+\alpha a/RTV^4+(c/RT^3V^2)(1+\gamma/V^2)\exp(-\gamma/V^2))$

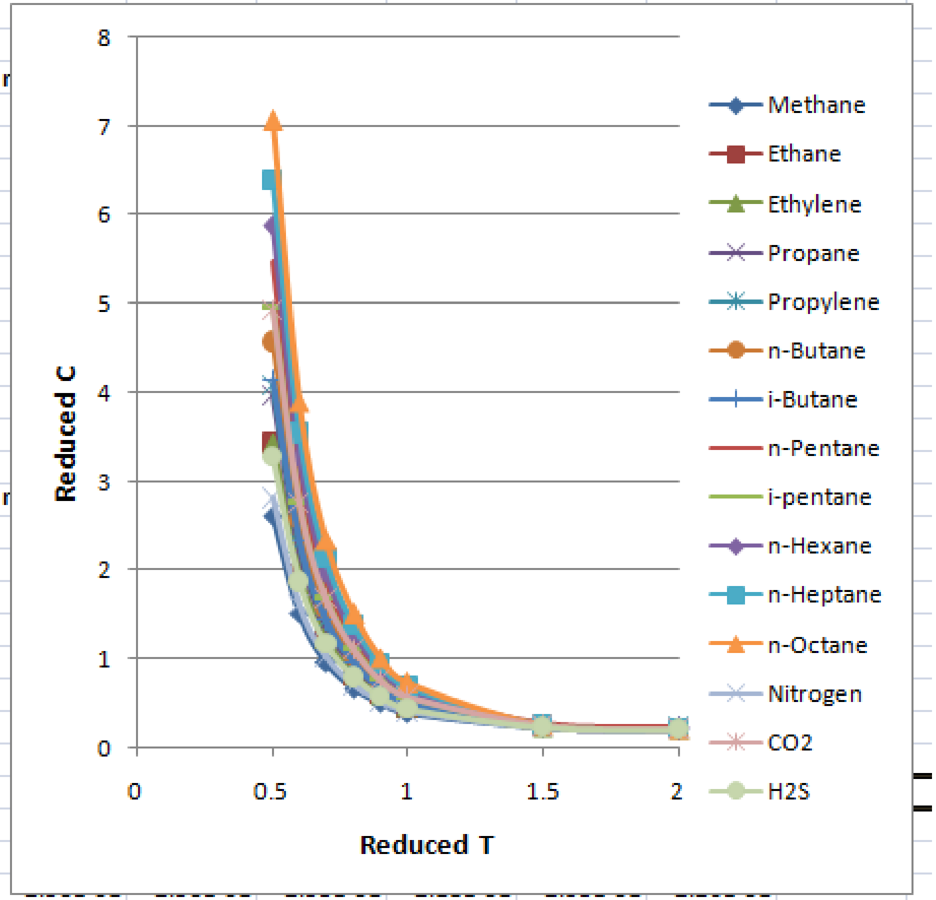
Cast it into virial equation of state:

$P=RT/V(1+(B_0-A_0/RT-C_0/RT^3)/V$
$+(b-a/RT+c/RT^3)/V^2+\alpha a/RTV^4+(c\gamma/RT^3V^6)$

Third virial coefficient is a monotonically decreasing function of T.

2^{nd} and 3^{rd} Virial coefficients from Starling





Cubic Virial Equation

Benedict-Webb-Rubin and Starling EOS can be reduced to:

$$P=RT/v+B/v^2+C/v^3+F/v^5$$

If F/v^5 is ignored, we have a cubic virial equation of state:

$$P=RT/v+B/v^2+C/v^3$$

Cubic Virial Equation

The cubic virial equation has all the nice properties of van der Waals equation of state, without the singularity at v=b.

$$Z=(RT/v)(1+B/v+C/v^2)$$

At critical temperature:

$B=-v_c$, $C=v_c^2/3$ and $Z_c=P_cv_c/RT_c=1/3$

Gas-Liquid Equilibrium

Gas and liquid phases are in equilibrium under saturation pressure:

$$P_{sat}=RT_{sat}(1+B/v+C/v^2)/v$$

It can be rearranged as:

$$1-(RT_{sat}/P_{sat})(1+B/v+C/v^2)/v = 0$$

Gas-Liquid Equilibrium

In the saturation region, the cubic equation has three roots, and can be written alternatively as:

$$(1-v_l/v)(1-v_m/v)(1-v_g/v)=0$$

which can be expanded as:

$$1-(v_l+v_g+v_m)/v+(v_lv_g+v_gv_m+v_mv_l)/v^2-v_lv_gv_m/v^3=0$$

Gas-Liquid Equilibrium

From these two identical equations:

$$1-(RT_{sat}/P_{sat})(1+B/v+C/v^2)/v=0$$

$$1-(v_l+v_g+v_m)/v+(v_l v_g+v_g v_m+v_m v_l)/v^2 -v_l v_g v_m/v^3=0$$

v_m , B, C and can be solved:

$$v_m= RT_{sat}/P_{sat}-v_l-v_g$$

$$B=-(v_l v_g+v_g v_m+v_m v_l)/(RT_{sat}/P_{sat})$$

$$C=v_l v_g v_m/(RT_{sat}/P_{sat})$$

Cubic Virial Equation

The cubic virial equation:

$$Z=(RT/v)(1+B/v+C/v^2)$$

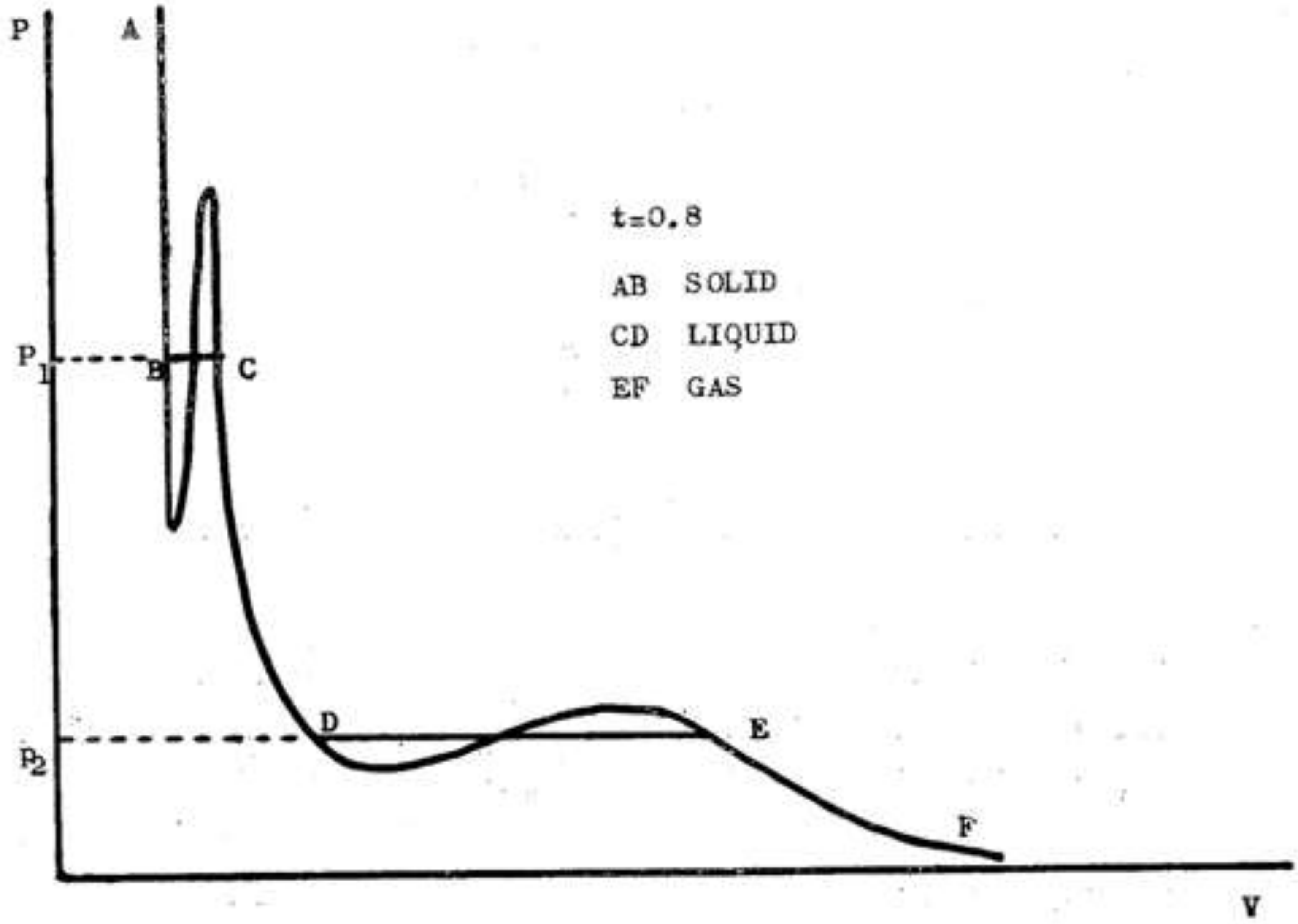
- More accurate than van der Waals EOS.
- No singularity.
- Compatible with Benedict-Webb-Rubin and Starling EOS.
- Virial coefficients can be derived from PVT data and from saturation properties.

Gas-Liquid-Solid Equilibrium

Cubic virial EOS can be extended for gas-liquid-solid equilibrium:
$P=(RT/V)(1+B/V+C/V^2+U/V^n+W/V^{2n})$

U/V^n depresses PVT isotherm, and W/V^{2n} pushes the isotherm up to form an S-shaped bend between v_s and v_l. The bend must be very sharp and very steep, requiring very high power factor n.

Gas-Liquid-Solid Equilibrium



Properties of Argon

Property	Value	Reduced Value
Critical Point Volume (dm^3/mole)	0.07459	1
Critical Point Temperature (^oK)	150.687	1
Critical Point Pressure (MPa)	4.863	1
Critical Compressibility ($Z_c=P_cV_c/RT_c$)	0.291	0.291
Triple Point Vapor Volume (dm^3/mole)	9.853	132.1
Triple Point Liquid Volume (dm^3/mole)	0.0282	0.378
Triple Point Solid Volume (dm^3/mole)	0.0246	0.330
Triple Point Temperature (^oK)	83.8058	0.553
Triple Point Pressure (MPa)	0.06889	0.0142

Gas-Liquid-Solid Equilibrium in Argon

The best virial EOS is with n=30:

$p=(t/vZ_c)(1-b/v+c/v^2-(v_u/v)^n+(v_w/v)^{2n})$

For Argon at the triple point

$t=0.553$, $p=0.0142$, $Z_c=0.291$

$v_s=0.330$, $v_l=0.378$

$b=3.424$, $c=1.152$

$n=30$, $v_u=0.3443$, $v_w=0.335$

Gas-Liquid-Solid Equilibrium in Argon

The best virial EOS is with n=30. The isotherm is plotted with three separated terms:

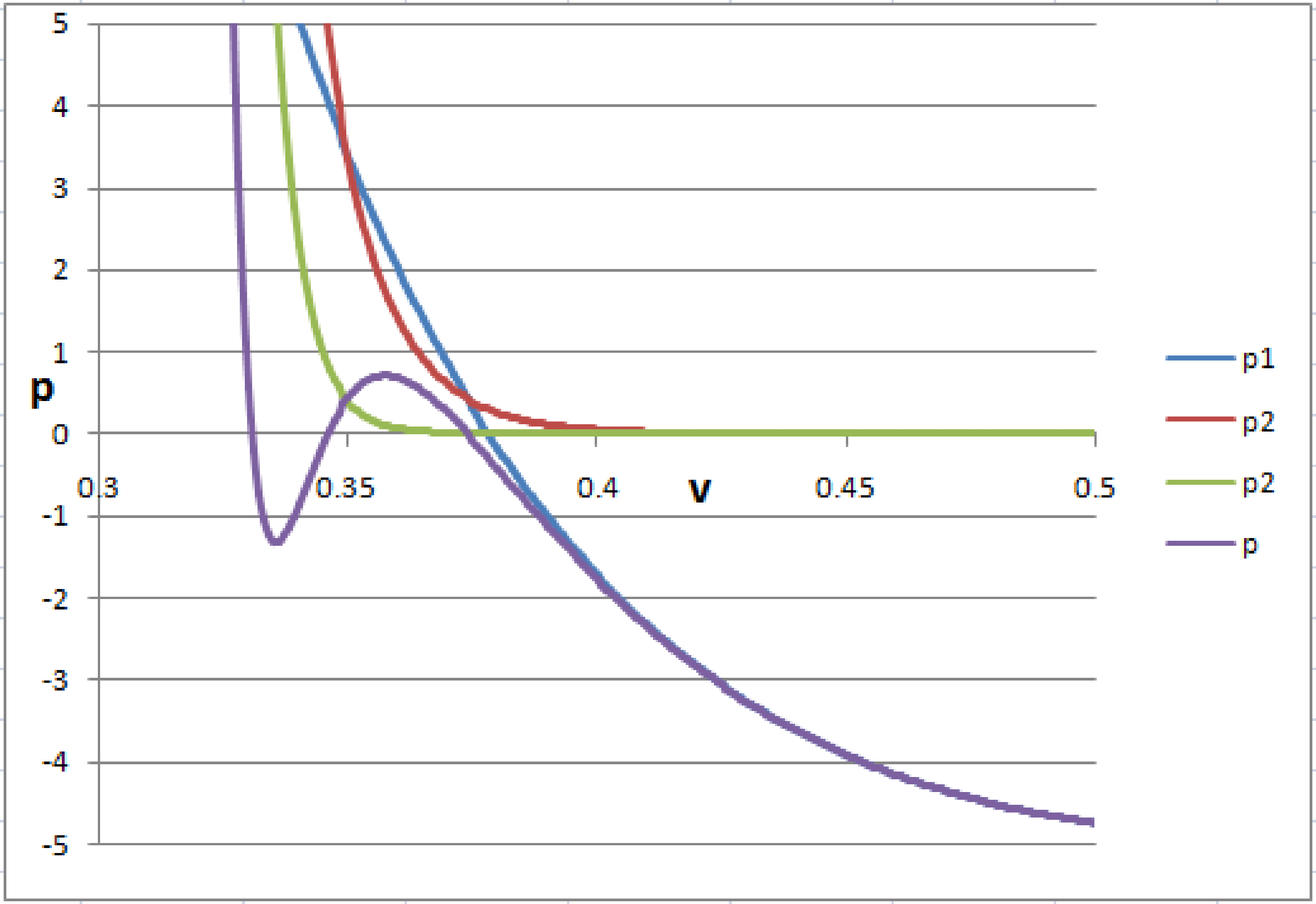
$p_1=(t/vZ_c)(1+b/v+c/v^2)$

$p_2=(t/vZ_c)(v_u/v)^n$

$p_3=(t/vZ_c)(v_w/v)^{2n}$

$p=p_1-p_2+p_3$

Gas-Liquid-Solid Equilibrium of Argon



Gas-Liquid-Solid Equilibrium

The best virial EOS is with n=30:

$$P=(t/vZ_c)(1-3.424/v+1.152/v^2 -(0.3443/v)^{30}+(0.3350/v)^{60})$$

Virial Coefficients

Virial EOS for gas-liquid-solid equilibrium:
$$P=(RT/V)(1+B/V+C/V^2+U/V^n+W/V^{2n})$$

- **B represents bimolecular attraction.**
- **C represents tri-molecular repulsion.**
- **U represents molecular attraction in liquid phase.**
- **W represents repulsion among molecules locked in crystal lattice.**

Virial Coefficients

n-2n potential well with n=30 seems excessive.

In liquid phase, an argon atom has 12 nearest neighbors, and up to 32 next nearest neighbors.

In solid phase, interacting neighbors are infinite in a crystal lattice.

Conclusions

- **3rd Virial coefficient is a monotonically decreasing function of T.**
- **A cubic virial EOS**
  $P = RT/v + B/v^2 + C/v^3$
  accurately prescribes gas-liquid equilibrium.
- **The cubic virial EOS can be extended**
  $P = (RT/V)(1 + B/V + C/V^2 + U/V^n + W/V^{2n})$
  for gas-liquid-solid equilibrium.

State of Virial Equations

- For every fluid, its cubic virial EOS has to be solved before considering high virial terms.
- Virial EOS can be solved with Excel. Multi-variable optimization is not necessary, and its results are not to be trusted.
- For the first time in history, gas-liquid-solid equilibrium is quantitatively represented by a virial equation of state.

Questions?

Thank You Very Much!