Statistical Mechanics Homework 7 — Ben Levy

#1 Pathria Problem 12.3

The critical point occurs when the first and second derivatives of pressure vanish. I begin be solving the given van der Waals equation of state for P *a la* equation 12.2.1, and taking the first and second derivative of P:

In[337]:= $P[T\_, v\_] = \frac{R\,T}{v-b} - \frac{a}{v^n};$

In[338]:= D[P[T, v], v]
D[P[T, v], {v, 2}]

Out[338]= $a\,n\,v^{-1-n} - \frac{R\,T}{(-b+v)^2}$

Out[339]= $a\,(-1-n)\,n\,v^{-2-n} + \frac{2\,R\,T}{(-b+v)^3}$

Now we must set the first and second derivatives to zero, and solve for $v = v_c$ and $T = T_c$. I had to get clever here. *Mathematica* couldn't just solve this system of equations, so instead I set the "n" in the exponents to be η, and plugged in η=1, 2, 3, ... , 9. Then I looked for the pattern. (it's pretty simple)

In[355]:= $\text{Table}\Big[\text{Solve}\Big[\Big\{a\,n\,v^{-1-\eta} - \frac{R\,T}{(-b+v)^2} == 0,\ a\,(-1-n)\,n\,v^{-2-\eta} + \frac{2\,R\,T}{(-b+v)^3} == 0\Big\},\ \{v, T\}\Big],\ \{\eta, 1, 9, 1\}\Big]$

Out[355]= $\Big\{\Big\{\Big\{v \to \frac{b+b\,n}{-1+n},\ T \to \frac{4\,a\,n}{(1+n)^2\,R}\Big\}\Big\},$
$\Big\{\Big\{v \to \frac{b+b\,n}{-1+n},\ T \to \frac{4\,(-a\,n+a\,n^2)}{b\,(1+n)^3\,R}\Big\}\Big\},\ \Big\{\Big\{v \to \frac{b+b\,n}{-1+n},\ T \to \frac{4\,a\,(-1+n)^2\,n}{b^2\,(1+n)^4\,R}\Big\}\Big\},$
$\Big\{\Big\{v \to \frac{b+b\,n}{-1+n},\ T \to \frac{4\,a\,(-1+n)^3\,n}{b^3\,(1+n)^5\,R}\Big\}\Big\},\ \Big\{\Big\{v \to \frac{b+b\,n}{-1+n},\ T \to \frac{4\,a\,(-1+n)^4\,n}{b^4\,(1+n)^6\,R}\Big\}\Big\},$
$\Big\{\Big\{v \to \frac{b+b\,n}{-1+n},\ T \to \frac{4\,a\,(-1+n)^5\,n}{b^5\,(1+n)^7\,R}\Big\}\Big\},\ \Big\{\Big\{v \to \frac{b+b\,n}{-1+n},\ T \to \frac{4\,a\,(-1+n)^6\,n}{b^6\,(1+n)^8\,R}\Big\}\Big\},$
$\Big\{\Big\{v \to \frac{b+b\,n}{-1+n},\ T \to \frac{4\,a\,(-1+n)^7\,n}{b^7\,(1+n)^9\,R}\Big\}\Big\},\ \Big\{\Big\{v \to \frac{b+b\,n}{-1+n},\ T \to \frac{4\,a\,(-1+n)^8\,n}{b^8\,(1+n)^{10}\,R}\Big\}\Big\}\Big\}$

Obviously:

$v_c = \frac{(n+1)\,b}{n-1}$ **and** $T_c = \frac{4\,a\,n\,(n-1)^{n-1}}{R\,b^{n-1}\,(n+1)^{n+1}}$

Now let's define these as variables

In[358]:= $vc = \frac{(n+1)\,b}{n-1};\ Tc = \frac{4\,a\,n\,(n-1)^{n-1}}{R\,b^{n-1}\,(n+1)^{n+1}};$

Then, to get P_c, all we must do is plug v_c and T_c into P:

In[360]:= **P[Tc, vc] // FullSimplify**

Out[360]= $a\left(2\,b^{-n}\,(-1+n)^{n}\,n\,(1+n)^{-1-n}-\left(\frac{b\,(1+n)}{-1+n}\right)^{-n}\right)$

Ok, *Mathematica* is kinda dumb. This simplifies to

$\boldsymbol{P_c = \frac{a}{b^n}\left(\frac{n-1}{n+1}\right)^n}$

I don't have time to figure out how to do the critical exponents.

$P = P_c(1+x)$, $V = v_c(1+y)$, $T = T_c(1+z)$

plug into equation of state, find $\alpha = f(y,z)$, and play around w/ the signs & limits of x, y, z ($>, =, < 0$)

15.22) Use self, $\langle e^f \rangle = e^{\langle f^2/2 \rangle}$, & $\langle [x(t) - x(0)]^2 \rangle = 2D|t|$ to solve