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Assignment 4
Q1

The critical point occurs when $\frac{\partial p}{\partial v} = \frac{\partial^2 p}{\partial v^2} = 0$

Finding $\frac{\partial p}{\partial v}$

$$p[v\_] = \frac{k\,T}{v-b}\,\text{Exp}\left[\frac{-a}{k\,T\,v}\right];$$

FullSimplify[p'[v]]

$$-\frac{e^{-\frac{a}{k T v}}\left(a\,(b-v)+k\,T\,v^2\right)}{(b-v)^2\,v^2}$$

Setting $\frac{\partial p}{\partial v} = 0$ we get:

$a\,(b-v)+k\,T\,v^2=0$

$\Rightarrow T = \frac{-a(b-v)}{v^2\,k}$

Finding and setting $\frac{\partial^2 p}{\partial v^2} = 0$

FullSimplify[p''[v]]

$$\frac{e^{-\frac{a}{k T v}}\left(a^2\,(b-v)^2-2\,a\,k\,T\,(b-2\,v)\,(b-v)\,v+2\,k^2\,T^2\,v^4\right)}{k\,T\,v^4\,(-b+v)^3}$$

$\Rightarrow a^2\,(b-v)^2-2\,a\,k\,T\,(b-2\,v)\,(b-v)\,v+2\,k^2\,T^2\,v^4 = 0$

Substituting in the expression for T in order to find v_c :

$\Rightarrow 3\,a^2\,(b-v_c)^2+\frac{2\,a^2\,(b-2\,v_c)\,(b-v_c)^2}{v_c} = 0$

$\Rightarrow 3\,v_c\ +2\,(b-2\,v_c)\ = 0$

$\Rightarrow v_c = 2\,b$

Substituting this back into T to find T_c:

$T_c = \frac{a}{4\,b\,k}$

Substituting this into p to find p_c:

$$p_c = \frac{k}{2\,b-b}\,\frac{a}{4\,b\,k}\,\text{Exp}\left[\frac{-a}{k\,2\,b}\,\frac{4\,b\,k}{a}\right]$$

$$p_c = \frac{a}{4\,b^2\,e^2}$$

$$\frac{p_c\,v_c}{k\,T_c} = \frac{\frac{a}{4 b^2 e^2}*2\,b}{k\,\frac{a}{4 b k}} = \frac{2}{e^2}$$

$$\overline{p} = \frac{p}{p_c} = \frac{2\,\overline{T}\,v_c}{2\,v-v_c}\,\frac{e^2}{2}\,\text{Exp}\left[\frac{-a}{k\,\overline{T}\,T_c\,\overline{v}\,v_c}\right] = \frac{2\,\overline{T}}{2\,\overline{V}-1}\,\frac{e^2}{2}\,\text{Exp}\left[\frac{-2}{\overline{T}\,\overline{v}}\right]$$

Finding the expansion coefficients:

Along the coexistance curve: $\overline{p}_g = \overline{p}_L$, and $\overline{T}_g = \overline{T}_L$

$$\frac{2\overline{T}}{2\overline{v}_g-1}\frac{e^2}{2}\text{Exp}\left[\frac{-2}{\overline{T}\,\overline{v}_g}\right]=\frac{2\overline{T}}{2\overline{v}_L-1}\frac{e^2}{2}\text{Exp}\left[\frac{-2}{\overline{T}\,\overline{v}_L}\right]$$

$$\text{Exp}\left[\frac{-2}{\overline{T}}\left(\frac{1}{\overline{v}_g}-\frac{1}{\overline{v}_L}\right)\right]=\frac{2\overline{v}_g-1}{2\overline{v}_L-1}$$

$$\overline{T}=\frac{-2\left(\frac{1}{\overline{v}_g}-\frac{1}{\overline{v}_L}\right)}{\text{Ln}\left(\frac{2\overline{v}_g-1}{2\overline{v}_L-1}\right)}$$

Setting $\overline{v}_g \approx 1+\epsilon/2$ and $\overline{v}_L \approx 1-\epsilon/2$

$$\overline{T}=\frac{-2\left(\frac{\overline{v}_L-\overline{v}_g}{\overline{v}_g\overline{v}_L}\right)}{\text{Ln}(1+\epsilon)-\text{Ln}(1-\epsilon)}=\frac{-2\left(\frac{1-\epsilon/2-(1+\epsilon/2)}{(1-\epsilon/2)(1+\epsilon/2)}\right)}{\epsilon-(-\epsilon)}=\frac{-2\left(\frac{-\epsilon}{1-\epsilon^2/4}\right)}{2\epsilon}=\frac{1}{1-\epsilon^2/4}$$

From Binomial Expansion:

$\overline{T}\approx 1+\epsilon^2/4$

Since $\epsilon = v_g - v_L$, if we rearrange we get:

$(v_g - v_L) \sim (T - T_c)^{-0.5}$

And so we get β=-0.5

Along an isotherm:

$$p = \frac{k\,T}{v-b}\,\text{Exp}\left[\frac{-a}{k\,T\,v}\right]$$

If we taylor expand this about $v = v_c$ we get (By definition of the critical point, the first and second derivatives are zero):

$$p = p_c + \frac{d^3\left(\frac{k\,T}{v-b}\,\text{Exp}\left[\frac{-a}{k\,T\,v}\right]\right)}{dv^3}\Bigg|_{v=v_c}(v-v_c)^3$$

$$p = p_c - \frac{\text{Exp}\left[-\frac{a}{k\,T\,v_c}\right]\left(a\,(b-v_c)+k\,v_c^2\right)}{(b-v_c)^2\,v_c^2}\,(v-v_c)^3$$

$$p - p_c = \frac{4\,k\,(-1+T_c)}{e^2\,v_c^2}\,(v_c-v)^3$$

And so we get δ=3

$$\kappa = \frac{-1}{v}\frac{\partial v}{\partial p}\Bigg|_T$$

Finding $\frac{\partial p}{\partial v}$, and evaluating this at $v = v_c$

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FullSimplify[D[k T/(v - vc/2) Exp[-Tc*2 vc k/(k T v)], v]]
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$$-\frac{4\,e^{-\frac{2\,Tc\,vc}{T\,v}}\,k\,\left(T\,v^2+Tc\,vc\,(-2\,v+vc)\right)}{v^2\,(-2\,v+vc)^2}$$

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FullSimplify[-(4 e^(-2 Tc vc/(T v)) k (T v^2 + Tc vc (-2 v + vc)))/(v^2 (-2 v + vc)^2) /. v → vc]
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$$\frac{4\,e^{-\frac{2\,Tc}{T}}\,k\,(-T+Tc)}{vc^2}$$

Hence we get:

$\kappa = \frac{-1}{v_c} \frac{v_c}{4\, e^{-\frac{2\,\mathrm{Tc}}{T}}\, k\,(-T+\mathrm{Tc})} = \frac{e^{2/T}}{4\,k} \frac{1}{T-T_c}$

And hence γ=1

Q2

Throughout this question, assume that a, b, c are functions of T.

b < 0

c > 0

Stable solutions occur when $\frac{\partial F}{\partial m} = 0$ and $\frac{\partial^2 F}{\partial m^2} > 0$

Solving $\frac{\partial F}{\partial m} = 0$ we get either m=0 or:

$a + 2\, b\, m^2 + 3\, c\, m^4 = 0$

$m^2 = \frac{-b \pm \sqrt{b^2 - 3\,a\,c}}{3\,c}$

If $b^2 - 3\,\mathrm{ac} < 0$, we will only have 1 real solution, m=0.

$a > \frac{b^2}{3\,c} > 0$

Suppose that $b^2 - 3\,\mathrm{ac} > 0$ and that $-b - \sqrt{b^2 - 3\,\mathrm{ac}} < 0$.

$\Rightarrow b^2 - 3\,\mathrm{ac} > b^2$

$\Rightarrow \mathrm{ac} < 0$

$\Rightarrow a < 0$

This means we have 3 solutions:

m=0

$m = \pm \sqrt{\frac{-b + \sqrt{b^2 - 3\,a\,c}}{3\,c}}$

Suppose that $b^2 - 3\,\mathrm{ac} > 0$ and that $-b - \sqrt{b^2 - 4\,\mathrm{ac}} > 0$.

$\Rightarrow b^2 - 3\,\mathrm{ac} < b^2$

$\Rightarrow \mathrm{ac} > 0$

$\Rightarrow a > 0$

This means we have 5 solutions:

m=0 or:

$m = \pm \sqrt{\frac{-b \pm \sqrt{b^2 - 3\,a\,c}}{3\,c}}$

I assume that a ≠ 0, as this case can be considered as the limit of the above cases.

Finding out which of these solutions are stable:

i.e. $\frac{\partial^2 F}{\partial m^2} > 0$

$\frac{\partial^2 F}{\partial m^2} = 2\,a + 12\,b\,m^2 + 30\,c\,m^4$

1 solution:

m=0 ⇒ $\frac{\partial^2 F}{\partial m^2} = 2\,a$

Since $a > \frac{b^2}{3c} > 0$, this solution is stable.

3 Solutions:

m=0 ⇒ $\frac{\partial^2 F}{\partial m^2} = 2\,a$

Since a<0, this is unstable.

$m = \pm\sqrt{\frac{-b+\sqrt{b^2-3ac}}{3c}}$

$\frac{\partial^2 F}{\partial m^2} = 2\,a + 12\,b\,\frac{-b+\sqrt{b^2-3\,a\,c}}{3\,c} + 30\,c\,\left(\frac{-b+\sqrt{b^2-3\,a\,c}}{3\,c}\right)^2$

$= 2\,a + 4\,b\,\frac{-b+\sqrt{b^2-3\,a\,c}}{c} + 10\,\left(\frac{b^2-2\,b\,\sqrt{b^2-3\,a\,c}+b^2-3\,a\,c}{3\,c}\right)$

$= 2\,a - \frac{4\,b^2}{c} + \frac{4\,b}{c}\,\sqrt{b^2-3\,a\,c} + \frac{20\,b^2}{3\,c} - \frac{20\,b}{3\,c}\,\sqrt{b^2-3\,a\,c} - 10\,a$

$= -8\,a + \frac{8\,b^2}{3\,c} - \frac{8\,b\,\sqrt{b^2-3\,a\,c}}{3\,c}$

Let $\Delta = \sqrt{b^2 - 3ac}$

$\frac{\partial^2 F}{\partial m^2} = \frac{8\,\Delta^2}{3\,c} - 8\,\frac{b\,\Delta}{3\,c}$

Since Δ > 0, c > 0, b < 0, both of these solutions have $\frac{\partial^2 F}{\partial m^2} > 0$, and so they are stable.

5 Solutions:

m=0 ⇒ $\frac{\partial^2 F}{\partial m^2} = 2\,a$

Since a>0, this is stable.

$m^2 = \frac{-b\pm\sqrt{b^2-3ac}}{3c}$

The + solution is the same as in the 3 solution case, and so we get these solutions to be stable.

Now consider only the - solution

$\frac{\partial^2 F}{\partial m^2} = 2\,a + 12\,b\,\frac{-b-\sqrt{b^2-3\,a\,c}}{3\,c} + 30\,c\,\left(\frac{-b-\sqrt{b^2-3\,a\,c}}{3\,c}\right)^2$

$= 2\,a + 4\,b\,\frac{-b-\sqrt{b^2-3\,a\,c}}{c} + 10\,\left(\frac{b^2+2\,b\,\sqrt{b^2-3\,a\,c}+b^2-3\,a\,c}{3\,c}\right)$

$= 2\,a - \frac{4\,b^2}{c} - \frac{4\,b}{c}\,\sqrt{b^2-3\,a\,c} + \frac{20\,b^2}{3\,c} + \frac{20\,b}{3\,c}\,\sqrt{b^2-3\,a\,c} - 10\,a$

$= -8\,a + \frac{8\,b^2}{3\,c} + \frac{8\,b\,\sqrt{b^2-3\,a\,c}}{3\,c}$

Let $\Delta = \sqrt{b^2 - 3ac}$

$\frac{\partial^2 F}{\partial m^2} = \frac{8\,\Delta^2}{3\,c} + 8\,\frac{b\,\Delta}{3\,c} = \frac{8\,\Delta}{3\,c}\,(\Delta + b)$

This is stable if Δ > -b

⇒ - 3 a c > 0

⇒ a<0

But for this solution, we have a > 0.

Hence it cannot be stable.

Sketches attached at the end.