HW #2   I.5

Gibbs free energy : $G = F + P_0 V$ is a minimum for a system at equilibrium with an external reservoir.

Any deviation is going to raise G :

$$\delta G = \delta F + P_0 \delta V > 0$$

$$\delta G \approx \left(\frac{\partial F}{\partial V}\right)_T \delta V + \frac{1}{2!}\left(\frac{\partial^2 F}{\partial V^2}\right)_T \delta V^2 + $$
$$+ \frac{1}{3!}\left(\frac{\partial^3 F}{\partial V^3}\right)_T \delta V^3 + \frac{1}{4!}\left(\frac{\partial^4 F}{\partial V^4}\right)_T \delta V^4 + P_0 \delta V > 0$$

Since $\frac{\partial F}{\partial V} = -P$, we can rewrite:

$$-P_0 \delta V - \frac{1}{2}\left(\frac{\partial P}{\partial V}\right)_T \delta V^2 - \frac{1}{3!}\left(\frac{\partial^2 P}{\partial V^2}\right)_T \delta V^3 -$$
$$- \frac{1}{4}\left(\frac{\partial^3 P}{\partial V^3}\right)_T \delta V^4 + P_0 \delta V > 0 \quad \text{or}$$

$$\frac{1}{2}\left(\frac{\partial P}{\partial V}\right)_T \delta V^2 + \frac{1}{3!}\left(\frac{\partial^2 P}{\partial V^2}\right)_T \delta V^3 + \frac{1}{4!}\left(\frac{\partial^3 P}{\partial V^3}\right)_T \delta V^4 < 0$$

At the critical point: $\frac{\partial P}{\partial V} = 0 \Rightarrow$

$$\frac{1}{3!}\left(\frac{\partial^2 P}{\partial V^2}\right)_T \delta V^3 + \frac{1}{4}\left(\frac{\partial^3 P}{\partial V^3}\right)_T \delta V^4 < 0$$

For arbitrary δV this will hold if

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} \equiv 0$$

and

$$\left(\frac{\partial^3 P}{\partial V^3}\right)_{T=T_c} < 0$$

(see L&L §)