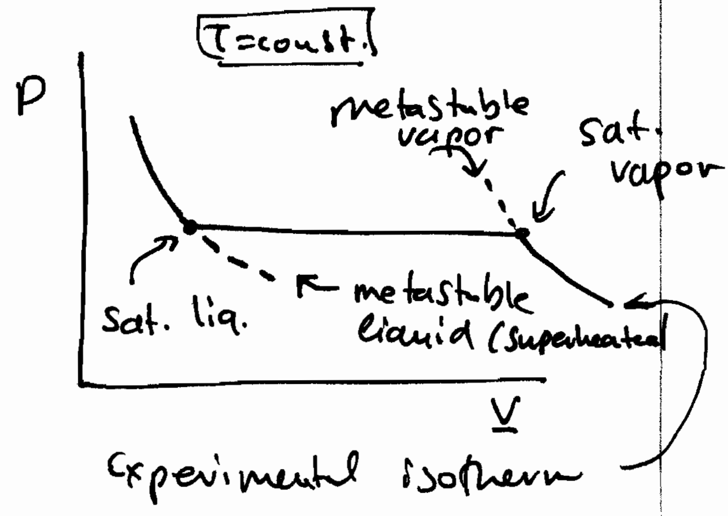
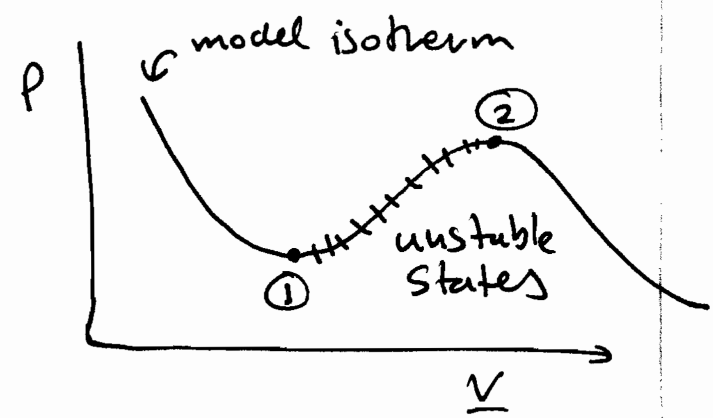
Metastability

(As seen in water superheating + supercooling experiments)



Equations of state (discussed in Ch 7) give smooth isotherms.



At points 1, 2

$$\left.\frac{\partial P}{\partial \underline{V}}\right)_T = 0 \quad \Big\{ \text{limit of Stability} \Big\}$$

between 1 and 2 are unstable

How can we determine the saturation points on the model isotherm?

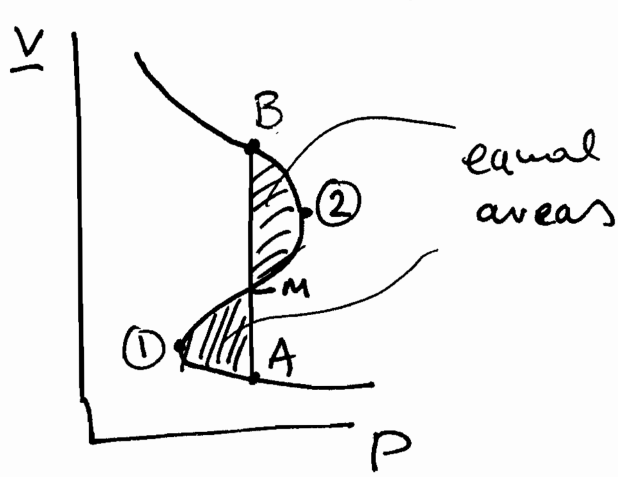
Condition of equilibrium: $\underbrace{T_I = T_{II}}_{\text{isotherm}}$ $\underbrace{P_I = P_{II}}_{\text{horiz. line}}$ $\underbrace{\mu_I = \mu_{II}}_{?}$

$$\left.\frac{\partial \mu}{\partial P}\right)_T = \left.\frac{\partial \underline{G}}{\partial P}\right)_T = \underline{V} \Rightarrow$$

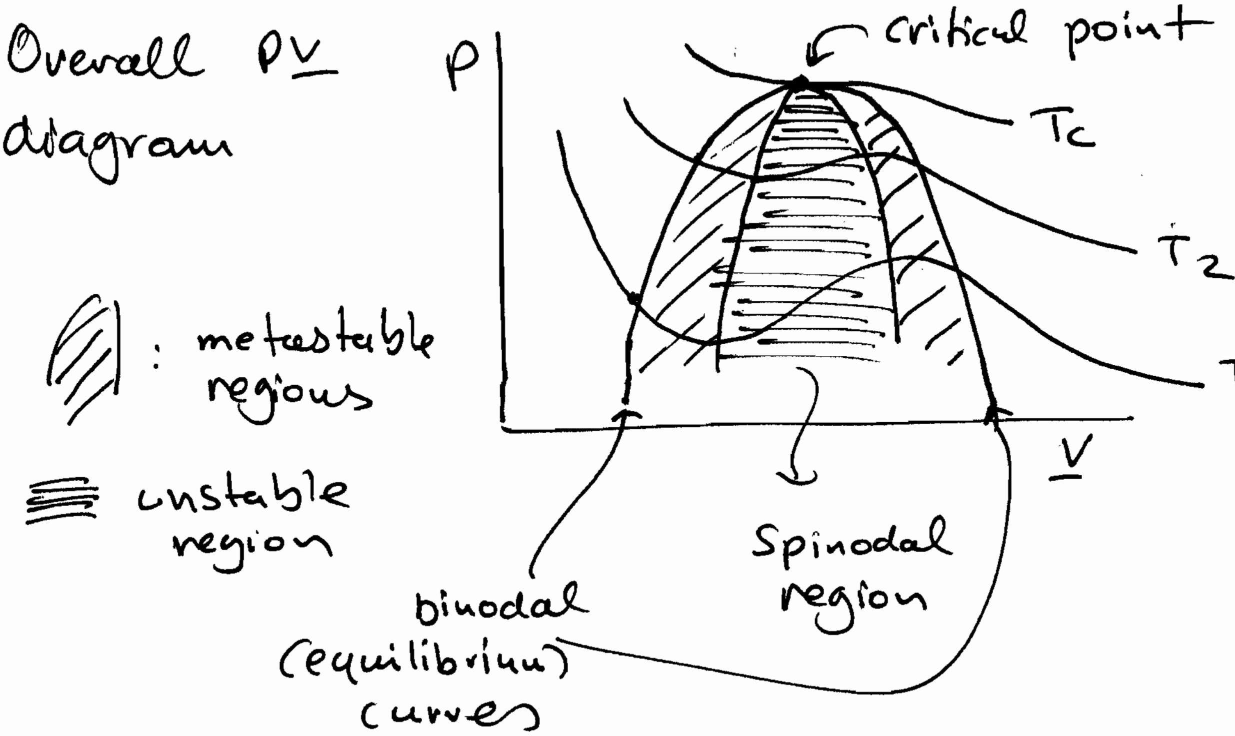
$$\Delta\mu = \int \underline{V}\, dP$$

Points A, B satisfy

$$\int_A^B \underline{V}\, dP = 0 \Rightarrow \mu_A = \mu_B$$



Overall $P\underline{V}$ diagram



At the critical point, $\underbrace{\left(\frac{\partial P}{\partial \underline{V}}\right)_T = \left(\frac{\partial^2 P}{\partial \underline{V}^2}\right)_T = 0}_{\text{Criticality conditions}}$

Strange things happen at critical points, which are <u>stable</u> limits of stability. Fluctuations and certain properties diverge.

e.g. $\left.\frac{\partial T}{\partial \underline{S}}\right)_P = \frac{T}{C_P} = 0 \Rightarrow C_P \to \infty$

Critical opalescence : YouTube cSli089x7UU

Unknown fluid, going down in T along critical isochore