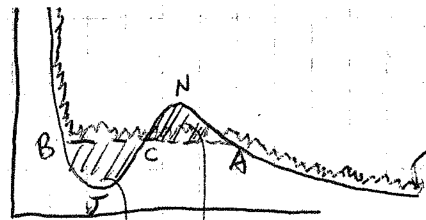



PV path taken by system if it is allowed to equilibrate every step of the way

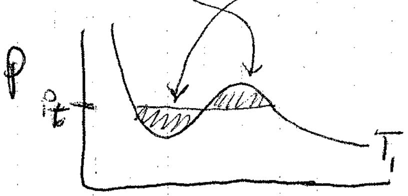
areas are equal

Since $g_L = g_g$ ~~throughout~~ transition

$$\int_{ANCJB} v\,dp = 0$$

$$\int_A^N v\,dp + \int_N^C v\,dp + \int_C^J v\,dp + \int_J^B v\,dp = 0$$

$$\left[\int_A^N v\,dp - \int_C^N v\,dp\right] + \left[-\int_J^C v\,dp + \int_J^B v\,dp\right] = 0$$




areas are equal

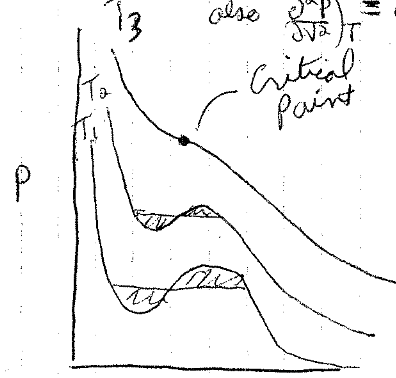
as T changes

at $T_c, P_c, V_c$ $\left.\frac{\partial p}{\partial V}\right)_T = 0$

gas is infinitely compressible (large density fluctuations)

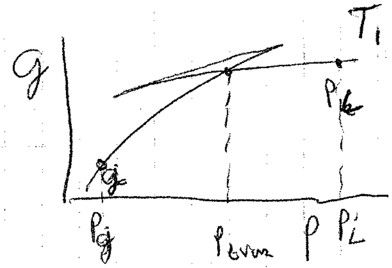
$T_c$ is the highest T where two phases exist

also $\left.\frac{\partial^2 p}{\partial V^2}\right)_T = 0$



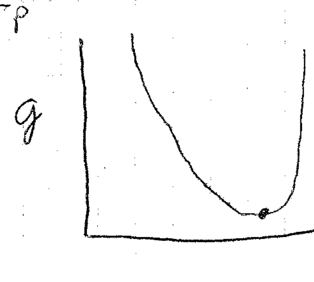

| | $T_c$, | $P_c$ |
|---|---|---|
| He | 5.2K | 2.25 Atm |
| $CO_2$ | 304K | 73 Atm |
| $H_2O$ | 647K | 218 Atm |

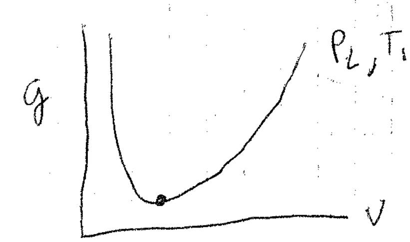
This collapses the V axis.

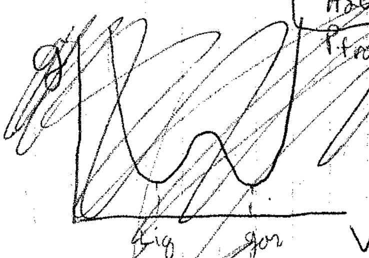




Next time do this on matlab in 3D



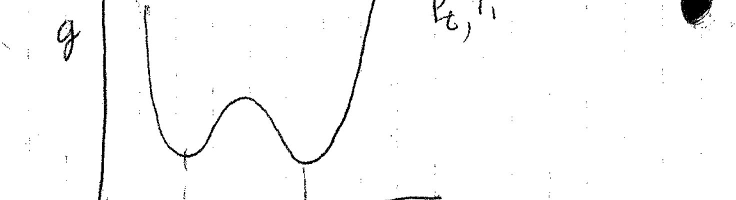



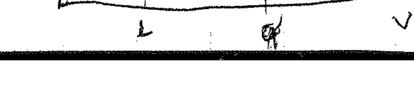

$P_{trans}; T_1$

~~not yet~~

~~how does g vs v at $P_{trans}$ change w/ temp~~

~~Note $P_{trans} = P_{trans}(T)$~~



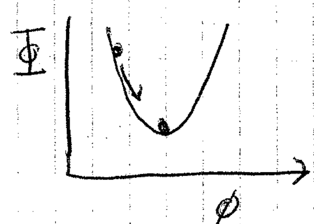



# First Order Phase Transitions

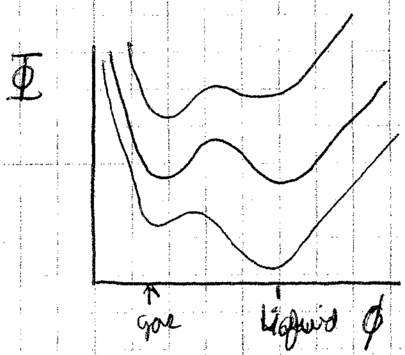
$\Phi$ some free energy  $\phi$ is our variable quantity

e.g.: Could be $G(V)$

If $\Phi(\phi)$ has a single minimum & $\phi$ for system can vary then system will decay towards the minimum




If $\Phi(\phi)$ has two minima usually one minimum is stable & the other is metastable. When they are equal system can switch between these phases without changing energy i.e. thermodynamic phase transition




↑ increasing T

which of these minima are stable?

$\Phi(\phi_1, \phi_2, \ldots)$

If any of the first derivatives $\frac{\partial \Phi}{\partial \phi_i}$ are discontinuous the transition is first order.

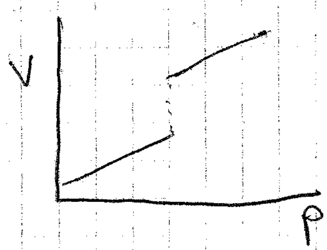
i.e. if there is a separation in $\phi$ b/w the two phases, is there is a hump between the states

Ex: G with constrained parameters $\phi_1 = T$ & $\phi_2 = P$

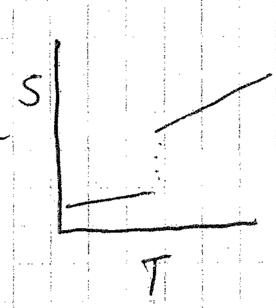
$$dG = -S\,dT + V\,dP$$

$$S = -\frac{\partial G}{\partial T}\Big)_P \qquad V = \frac{\partial G}{\partial P}\Big)_T$$

if



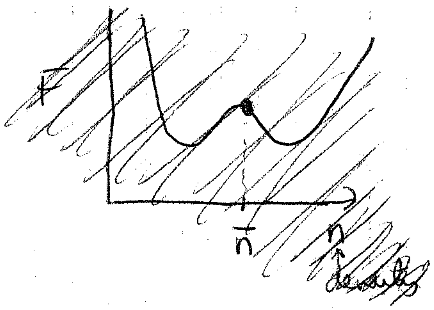

or

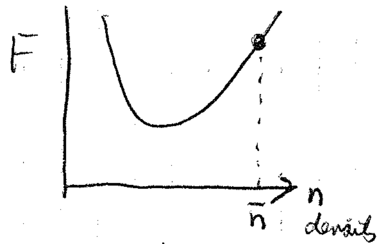



If all derivatives are continuous but second ~~order~~ derivative is discontinuous — 2nd order phase transition occurs at the critical pt. $T_c, P_c, V_c$

So far we have let $\phi$ vary so the system can choose which state to go into. What if $\phi$ is constrained?

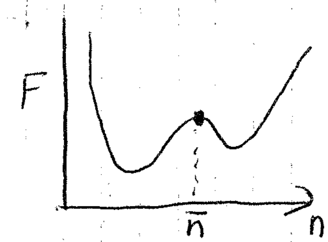
Ex: Hold volume constant (only allow exchange of heat) & cool gas. Then we will use the Helmholtz Free energy



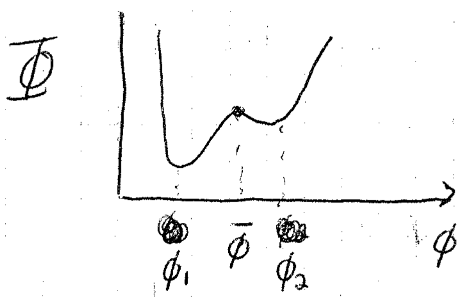




System is stuck

what if




What does the system do? Notice that we can seperate system into two phases & lower F. How does the system go about doing this?




$$\bar{\phi} = x\phi_1 + (1-x)\phi_2$$

what is the optimal choice for $\phi_1$ & $\phi_2$

$$\bar{\Phi}(\phi_1, x) = x\,\Phi(\phi_1) + (1-x)\,\Phi(\phi_2)$$

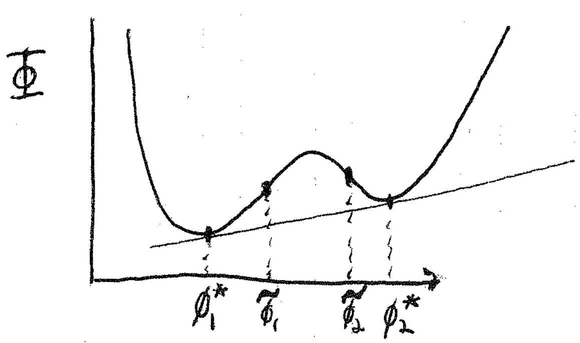
$$= x\,\Phi(\phi_1) + (1-x)\,\Phi\left(\frac{\bar{\phi} - x\phi_1}{1-x}\right)$$

minimize with respect to $\phi_1$: $\boxed{x\Phi'(\phi_1) - x\Phi'(\phi_2) = 0}$ slopes of $\Phi$ are the same at $\phi_1$ & $\phi_2$

minimize with respect to $x$: $\Phi(\phi_1) - \Phi(\phi_2) - (1-x)\Phi'(\phi_2)\left(\frac{\phi_1}{1-x} - \frac{\bar{\phi} - x\phi_1}{(1-x)^2}\right) =$

$$\boxed{\Phi'(\phi_2) = \frac{\Phi(\phi_1) - \Phi(\phi_2)}{\phi_1 - \phi_2}}$$

Both Conditions are satisfied by drawing a double tangent to the curve

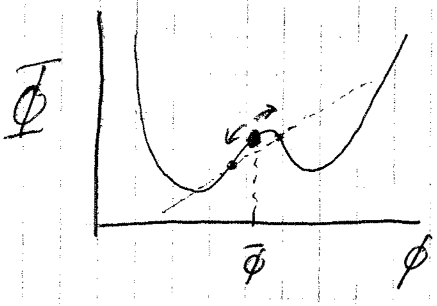



$\tilde{\phi}_1$ & $\tilde{\phi}_2$ designate points of inflection

The way systems arrive at $\phi_1^*$ & $\phi_2^*$ depend on initial Condition

# Nucleation & Growth vs. Spinodal decomposition

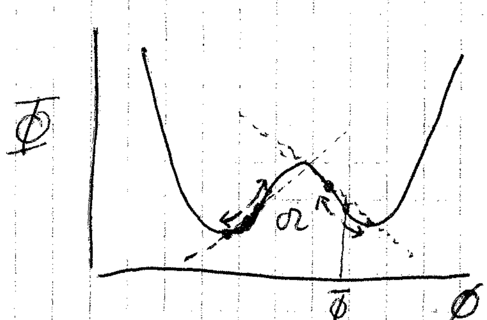
## Spinodal decomposition:




if system starts with $\bar{\phi}$ between the inflection points $\tilde{\phi}_1$ & $\tilde{\phi}_2$ Then local phase separation lowers ave free energy

Show movie of Spinodal decomposition

## Nucleation & growth




If System starts with $\bar{\phi}$ between an inflection point & a minimum

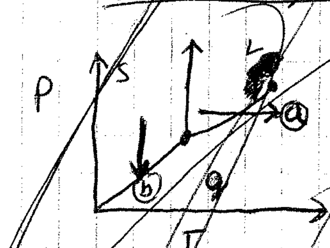
Then local phase separation Raises the ave Free energy.

Here in order to phase separate, System must undergo Nucleation & growth of one phase inside the other.

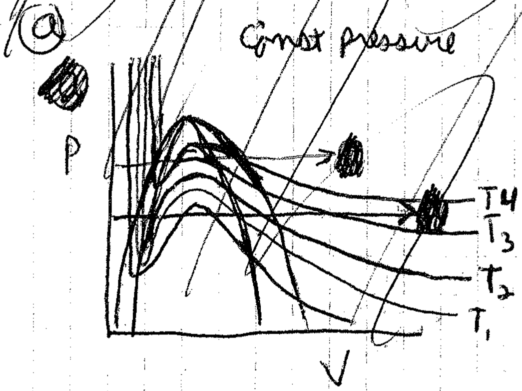
Show movie of nucleation & growth

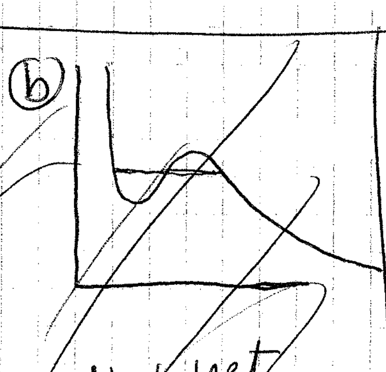
---

## Summary Examples




Use PV diagrams to explain what is going on




Not yet

## Order Parameter

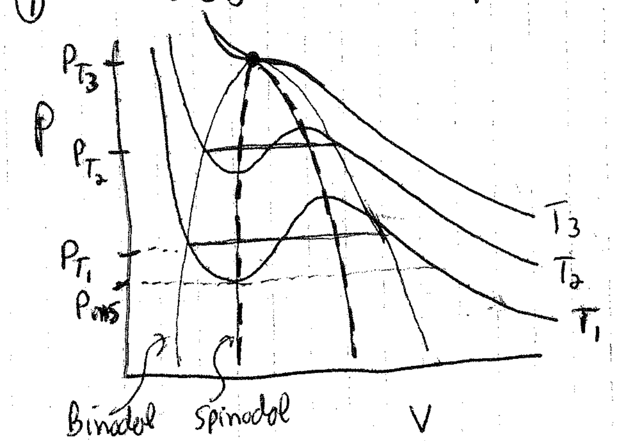
The additional variable we need to specify for new system in order to define the thermodynamic state of the new system

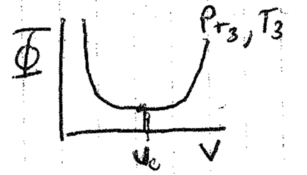
Ex: 1) Gas-Liquid $\quad \rho$ density

2) Binary-mixture $\quad \rho_1, \rho_2$

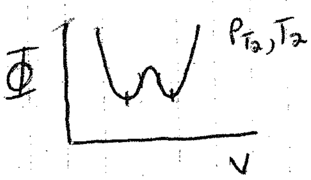
3) Solid-Liquid $\quad$ peaks in x-ray or orientational order etc.

① Lets match up free energy diagrams w/ P v isotherms



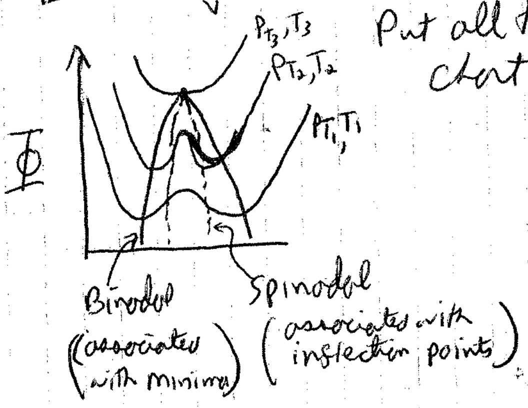

one minimum



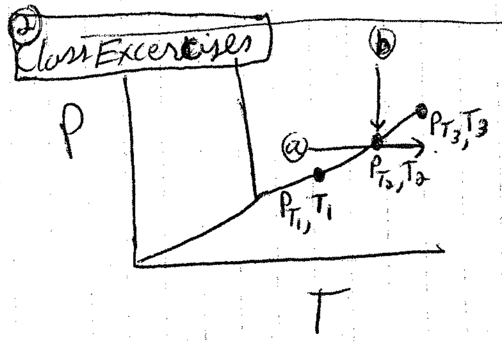

two close set minima


two minima well separated in V

Put all three curves on one chart




② Class Excercises




ⓐ Boiling a pot of water at atmospheric pressure

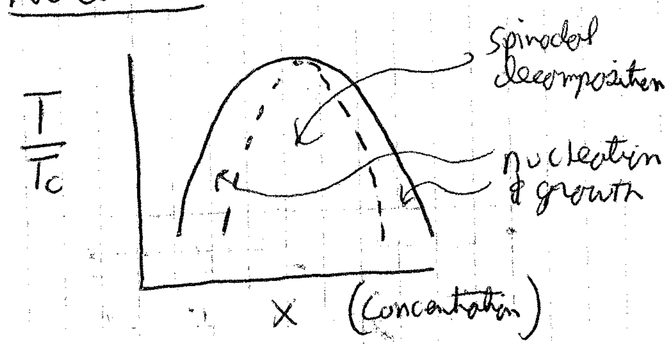
ⓑ two choices

I) we have $\bar{V}$ such that system is in the spinodal region. Then we have spinodal decomposition

II) we have $\bar{V}$ such that system is in between the Binodal & Spinodal

Then we have nucleation and growth

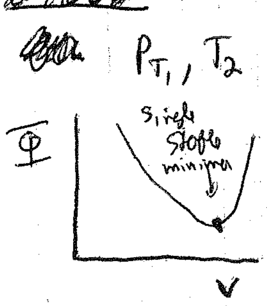
③ For culture! Binary mixtures:

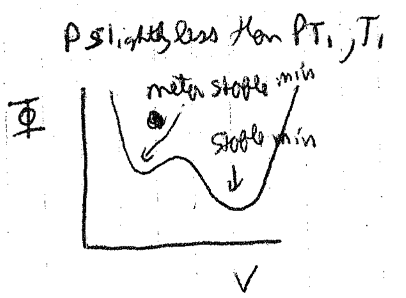


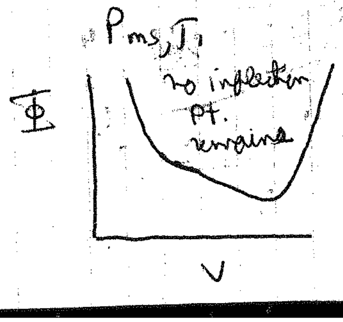

Show demo from Phil

Work w/ partner in class

draw free energy for:



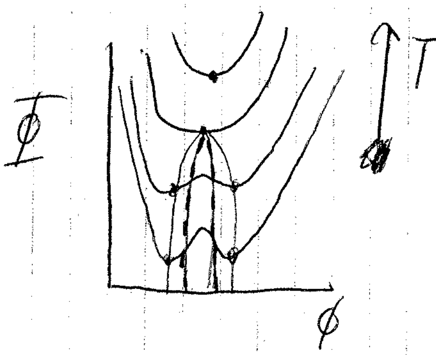



# 2nd Order or Continuous Phase Transitions

Minimum of Free energy evolves smoothly into two minima

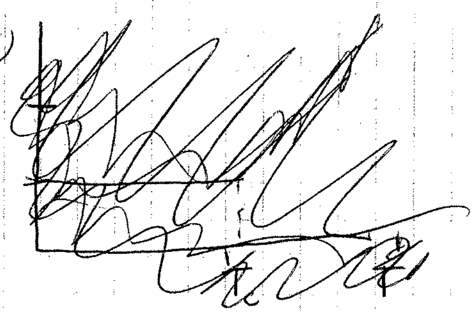
Ex quenched down in T at const $V_c$

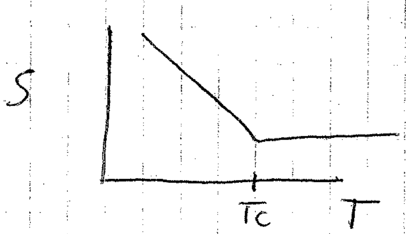



Mean field approx: minima move apart as $(T-T_c)$

For example:

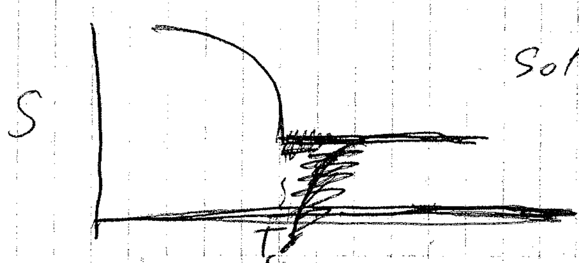
$$S = -\frac{\partial \Phi(\phi)}{\partial T}$$






Continuous but second derivatives $C_v$ & $C_p$ are discontinuous at $T_c$

typically this looks more like




so that the heat capacity diverges at $T_c$

---

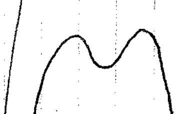
<u>Landau theory</u>: Generally to get the shape of the curves we have been discussing you need to be able to write the potential as $\Phi(\phi) = \Phi_0 + \frac{1}{2}a\phi^2 + \frac{1}{4}b\phi^4 + \frac{c}{6}\phi^6$

Possible examples:

all coeff +

all coeff −

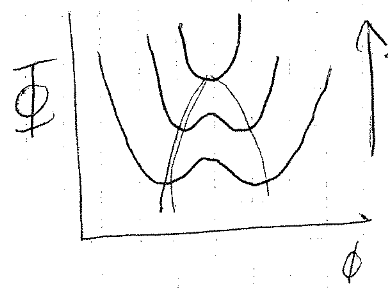
$a^+$ $b^-$ $c=0$



$a^-, b^+$ $c=0$

# Symmetry Breaking

If we start w/ a continuous phase transition w/o a constrained variable $\phi$




How does system decide which minima to choose?

typically $\Phi = \Phi_0 + \frac{a}{2}\phi^2 + \frac{b}{4}\phi^4 + \dots$ all even terms.

In order to break the degeneracy one must add a linear or odd term

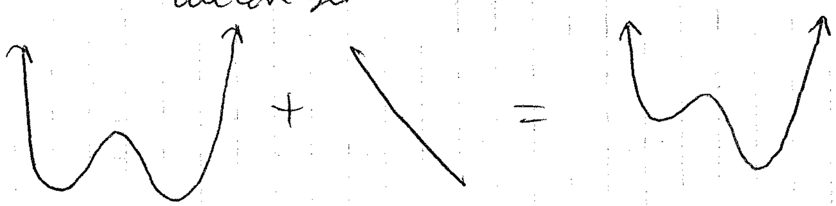
Ex: spin model: above $T_c$ spins are random.
below $T_c$ spins point ~~up or down~~ in a particular direction

in the absense of an H field the system can go either way

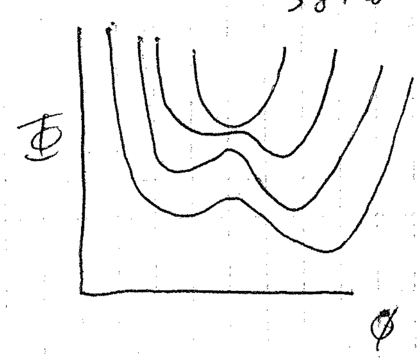
by adding a symmetry breaking field

$$\Phi = \Phi_0 + \frac{a}{2}\phi^2 + \frac{b}{4}\phi^4 + \dots - \eta\phi$$

we can set:




So transition becomes:




If we take system down from high T we continuously move into the lower min.

If on the other hand we are already at low T & switch $\eta \to -\eta$ the minima will switch & we get a first order phase transition

$\boxed{\text{Done w/ Thermo}}$