

# Lecture 13

27.02.2019

Mean field theory, Phase transitions

# Configuration probability distribution

Probability for a microstate with a spatial configuration of particles at positions  $\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N$

$$P_N(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{Q_N} e^{-\beta U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)}$$

For homogeneous and isotropic systems  $P_N(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{Q_N} \prod_{i < j} e^{-\beta u(r_{ij})}$

- **PROBLEM!**

$P_N(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$  is a multidimensional function, and generally difficult to compute

- **SOLUTION 2:**

- Mean field approximation: Each particle interacts with a constant effective potential field «mean interaction potential» induced by all the other particles
- Thermodynamic properties, like *pressure*, *internal energy*, can be expressed in terms of these effective potential

# Mean-field approximation: interaction potential

The interaction potential on a particle varies from particle to particle

In the mean field approximation, we assume that all particles experience the same effective potential field

$$\sum_{j \neq i} u(r_{ij}) \rightarrow \bar{u} = \bar{u}(\rho)$$

$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_i \sum_{i \neq j} u(r_{ij}) = \sum_{i=1}^N \bar{u} = N\bar{u}$$

Configurational partition function

$$Q_N = \int d\vec{r}_1 \cdots d\vec{r}_N e^{-\beta U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)} = \int d\vec{r}_1 \cdots d\vec{r}_N e^{-\beta N\bar{u}}$$

$$Q_N = Q_1^N$$

$$Q_1 = \int d\vec{r}_1 e^{-\beta \bar{u}} = (V - Nb)e^{-\beta \bar{u}}, \quad b \text{ is the particle exclusion volume}$$

# Mean-field approximation and self-consistent equation

Canonical partition function

$$Z_N = \frac{1}{N!} \frac{Q_N}{\Lambda^{3N}}, \quad Q_N = (V - Nb)^N e^{-N\beta\bar{u}}$$

Helmholtz free energy

$$F_N = -NkT \left[ \ln \left( \frac{(V - Nb)}{N\Lambda^3(T)} \right) - \beta\bar{u}(\rho) + 1 \right]$$

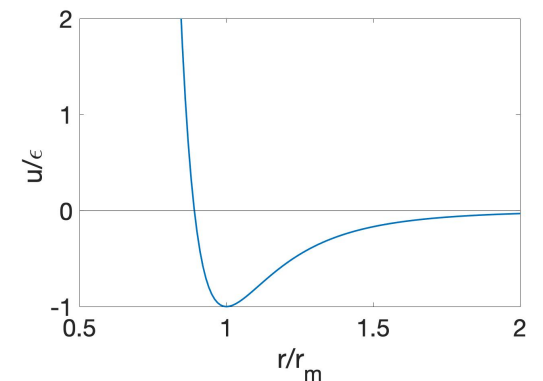
- How do we determine the mean interaction potential,  $\bar{u}$ ?  $\bar{u}$  is determined by the **self-consistent equation**

$$\bar{u} = \frac{\langle U_N \rangle}{N} = \frac{\rho}{2} \int d\vec{r} u(r) g(r)$$

Lenard-Jones type of interaction (strong repulsion on short distance, weak long range attraction):

$$\bar{u} = 2\pi\rho \int_0^\infty dr r^2 u(r) e^{-\beta u(r)} = \rho 2\pi \int_{r_m}^\infty dr r^2 u(r)$$

$$\bar{u}(\rho) = -\rho a = -\frac{Na}{V}, \quad a > 0$$



# Equation of state: Mean-field approximation

$$F_N = -NkT \left[ \ln \left( \frac{(V - Nb)}{N\Lambda^3(T)} \right) + \frac{Na}{kTV} + 1 \right]$$

$$F_N = \underbrace{-NkT \left[ \ln \left( \frac{V}{N\Lambda^3(T)} \right) + 1 \right]}_{\text{ideal}} \underbrace{- NkT \ln \left( 1 - \frac{Nb}{V} \right)}_{\text{Entropic correction from exclusion volume}} \underbrace{- \frac{N^2 a}{V}}_{\text{Energy correction from attraction forces}}$$

ideal

Entropic correction from  
exclusion volume

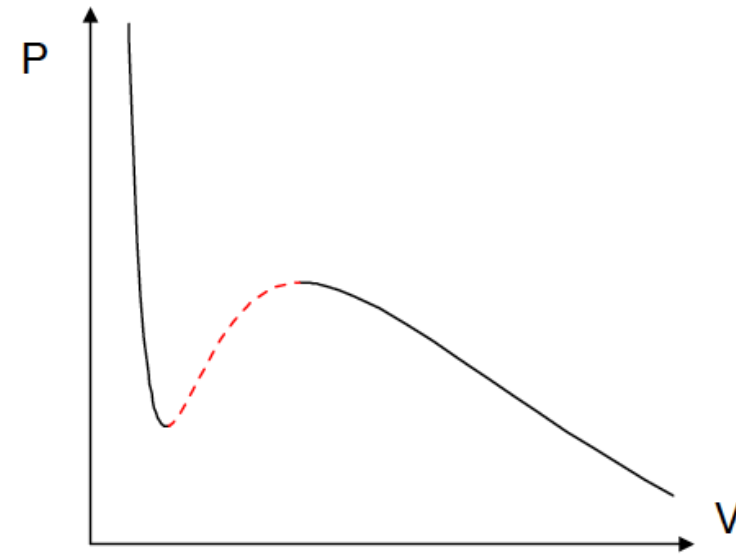
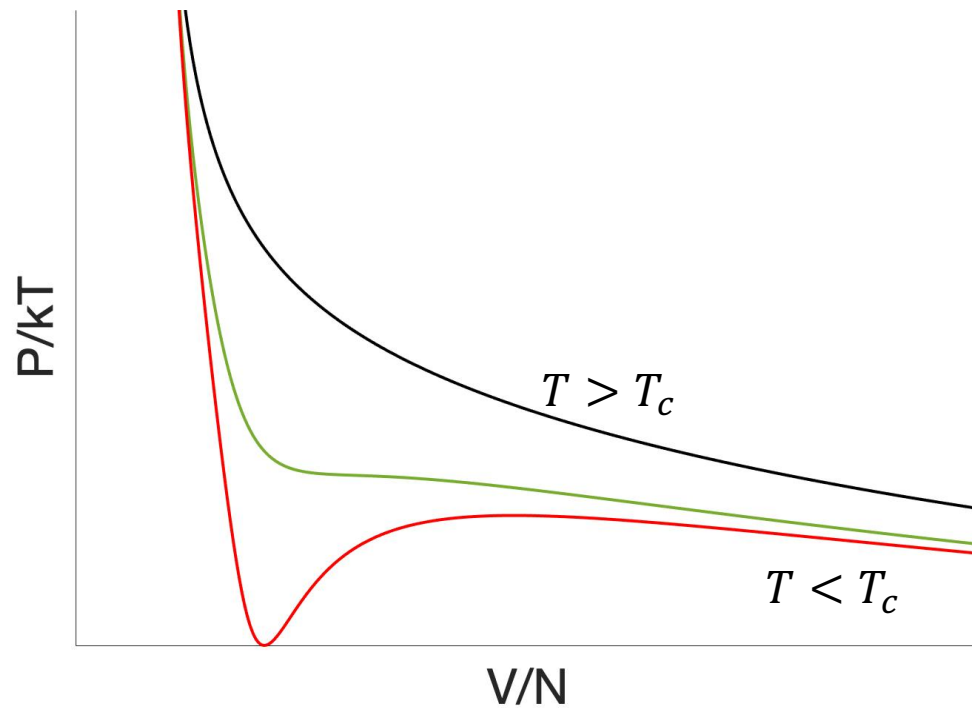
Energy correction from  
attraction forces

$$P = -\frac{\partial F}{\partial V} = \frac{kT}{Q_N} \frac{\partial Q_N}{\partial V}$$

$$P = kT \left( \frac{N}{V - Nb} - \frac{a N^2}{kT V^2} \right)$$

# Van der Waals: Mean-field approximation

$$\frac{P}{kT} = \frac{N}{V - Nb} - \frac{a N^2}{kT V^2}$$



$P(V)$  curve becomes non-monotonic

$\frac{\partial P}{\partial V} > 0$  is an unstable branch because it corresponds to

$$\frac{\partial^2 F_N}{\partial V^2} < 0$$

Helmholtz free energy becomes concave (unstable region)

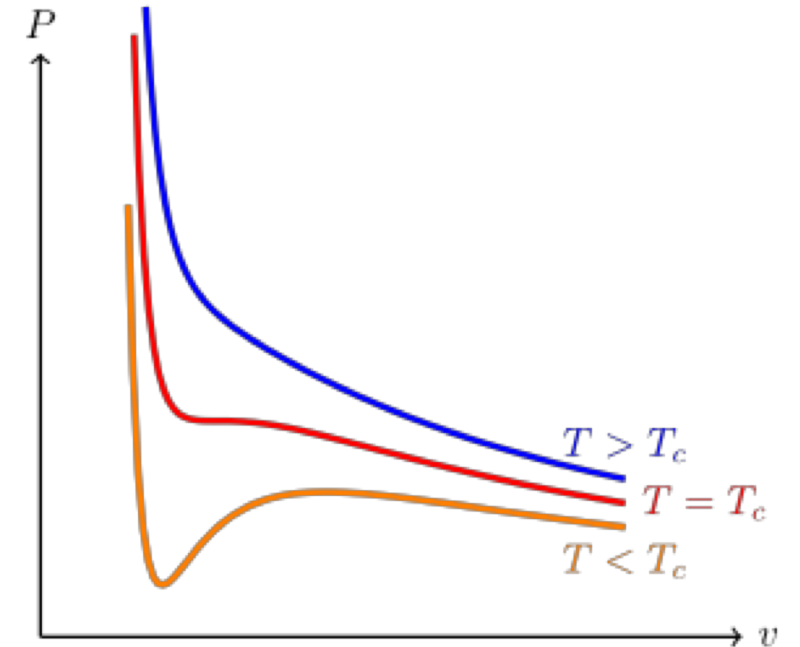
# Van der Waals fluids at the critical point $T_c$

Critical point defined as the inflection point of the isotherm in the  $P - V$  diagram:

$$\frac{\partial P}{\partial V} = 0, \quad \frac{\partial^2 P}{\partial V^2} = 0$$

*Applied to the van der Waals equation of state*

$$P_c = \frac{a}{27b^2}, \quad T_c = \frac{8a}{27bk}, \quad V_c = 3b$$



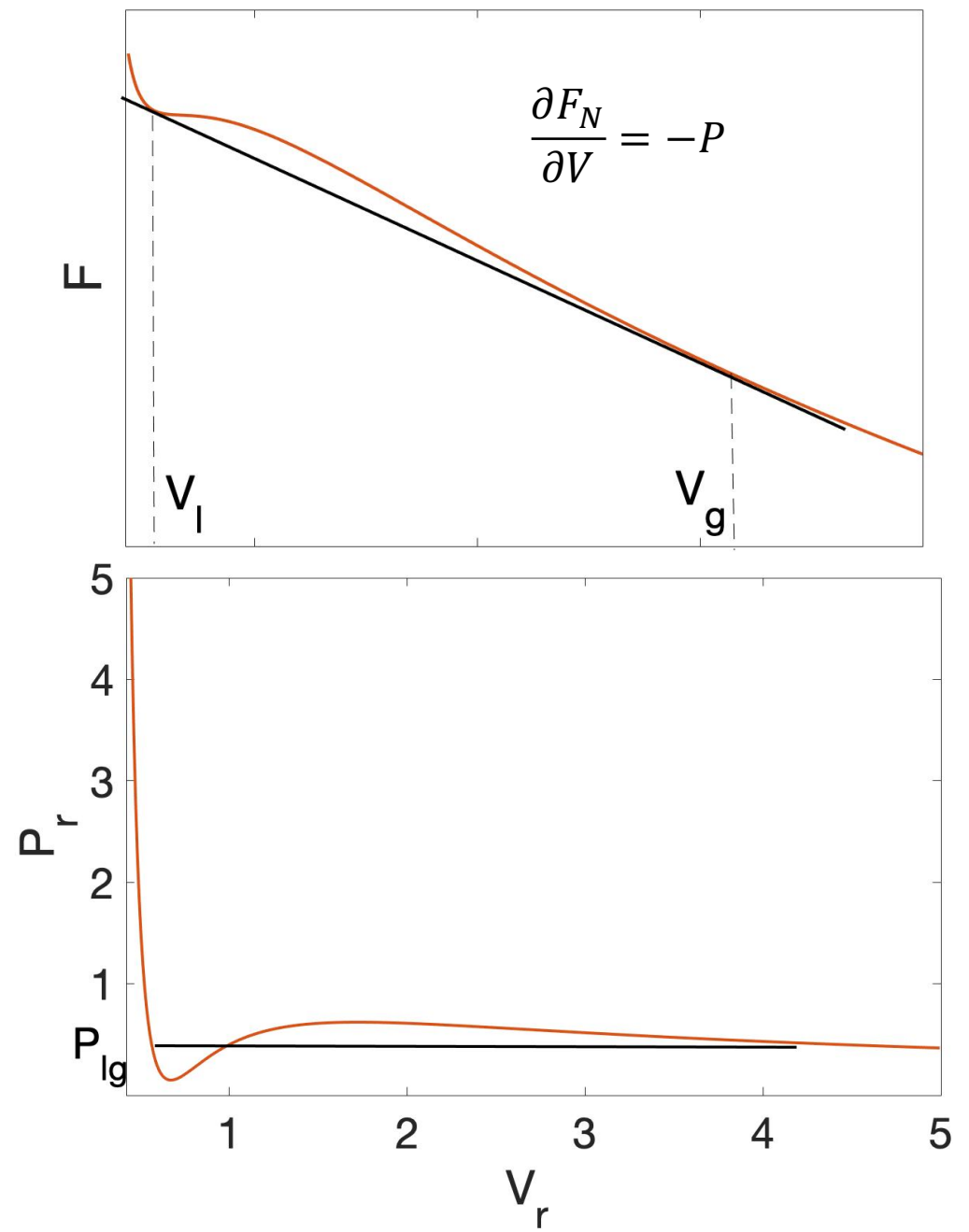
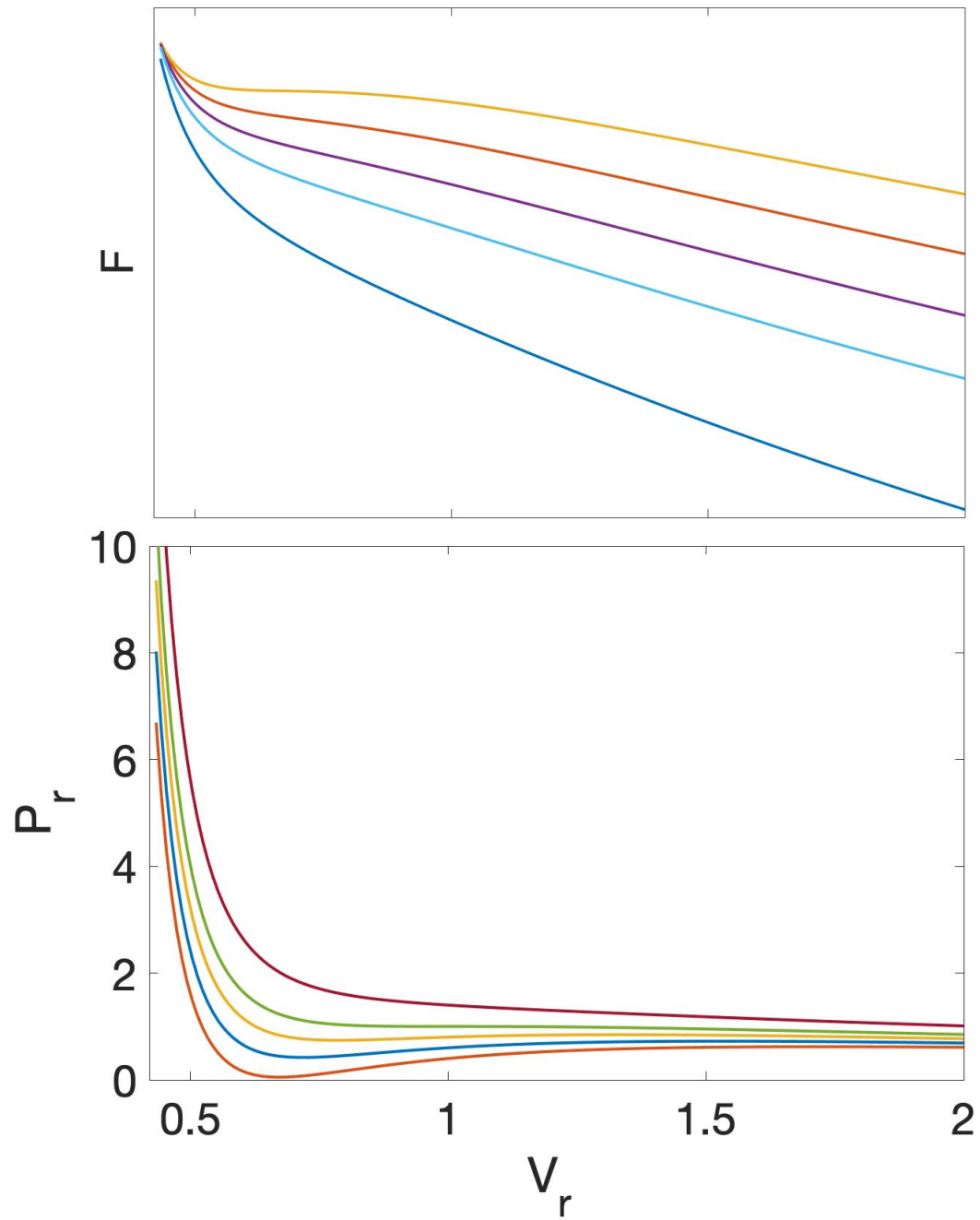
Rescaled  $P, V, T$  in units of the critical  $P_c, V_c, T_c$

$$P_r = \frac{P}{P_c}, \quad T_r = \frac{T}{T_c}, \quad V_r = \frac{V}{V_c}$$

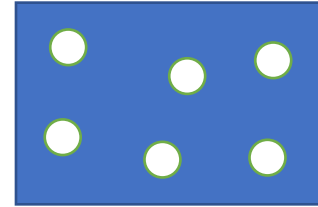
$$F_N \approx -T_r \left[ \ln \left( V_r - \frac{1}{3} \right) + \frac{3}{2} \ln(T_r) + \frac{9}{8} \frac{1}{V_r T_r} + 1 \right]$$

$$P_r = \frac{8 T_r}{3 V_r - 1} - \frac{3}{V_r^2}$$

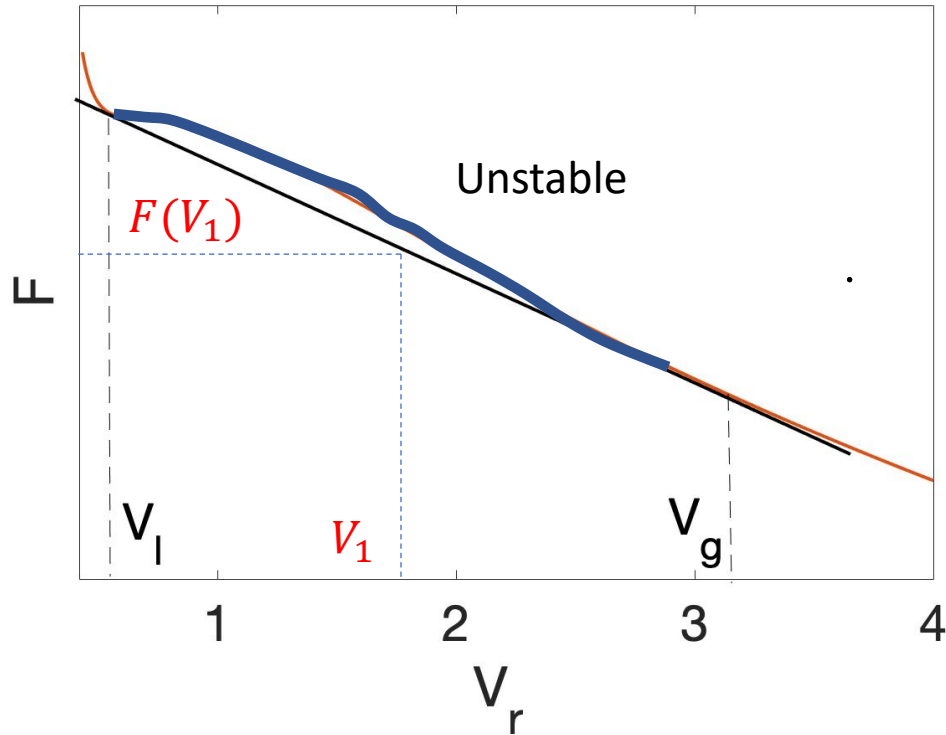




# Van der Waals: phase transition below $T_c$



Phase separation



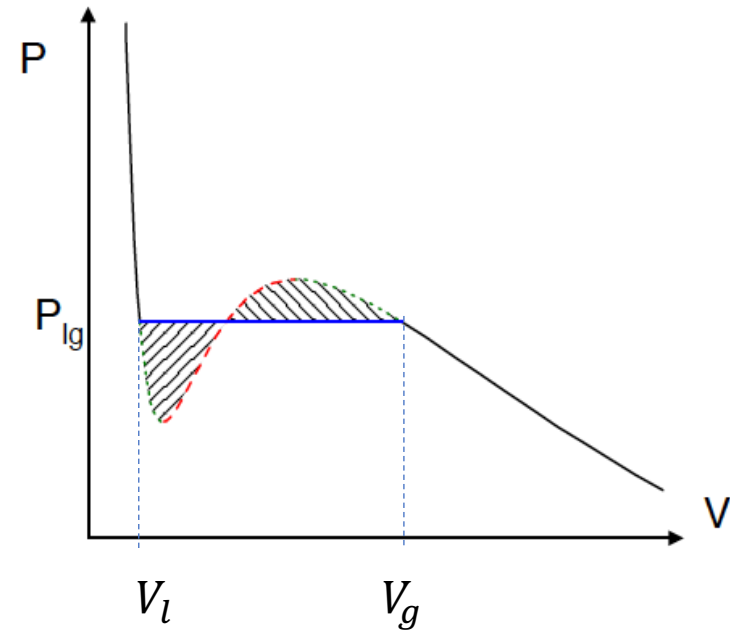
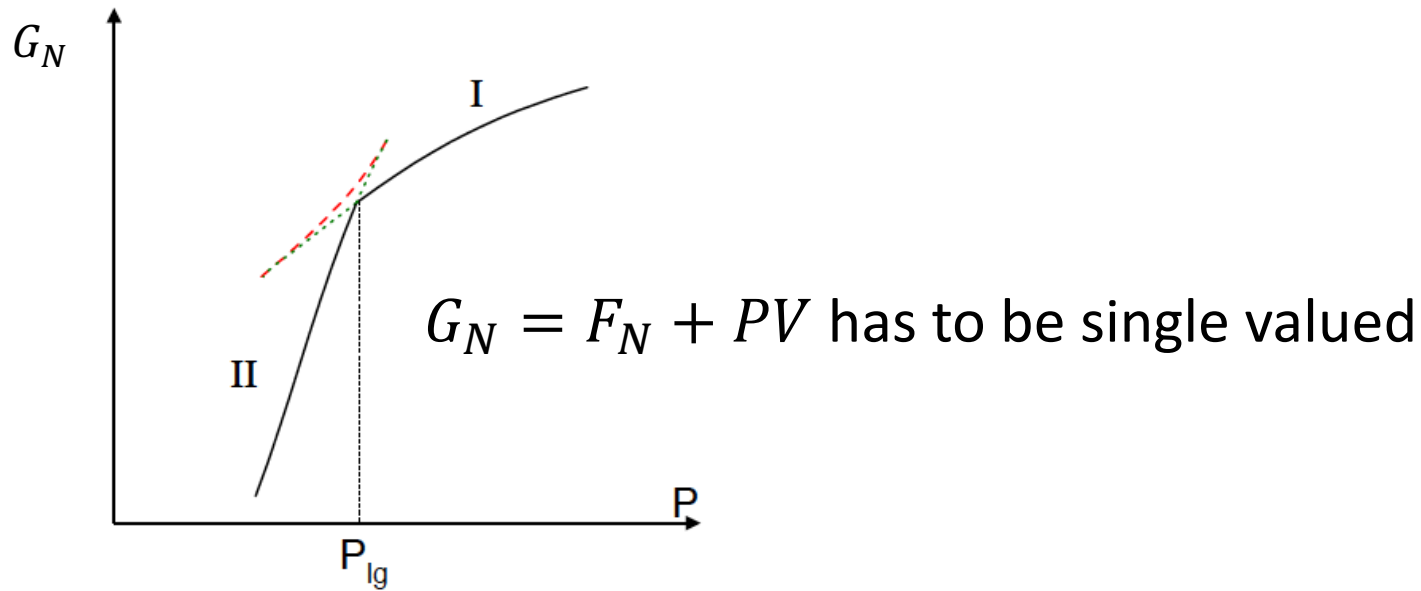
*Liquid phase and the gas phase are at equilibrium  
and the state of their mixture is determined by*

Common tangent construction

$$F_N(V_1) = \frac{N_l}{N} F_{N_l}(V_l) + \frac{N_g}{N} F_{N_g}(V_g)$$

$$V_1 = \frac{N_l}{N} V_l + \frac{N_g}{N} V_g, \quad N = N_l + N_g$$

# Fluid mixture below $T_c$



Maxwell equal-area construction

$$\oint_{P_{lg}} dG_N = 0$$

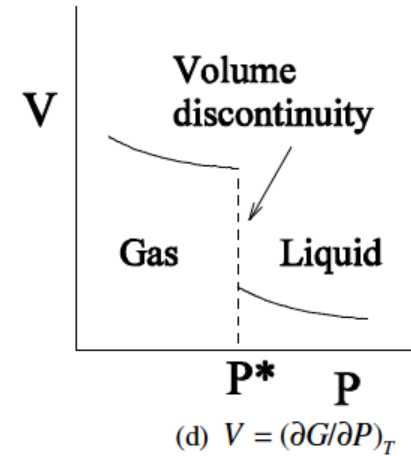
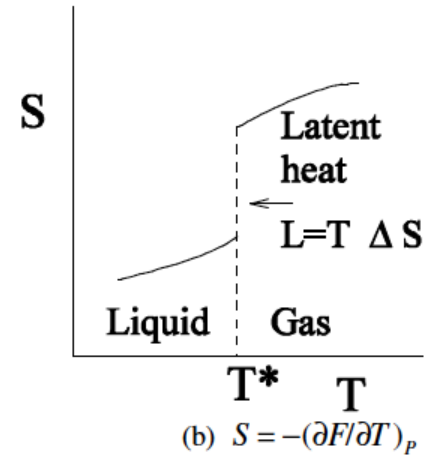
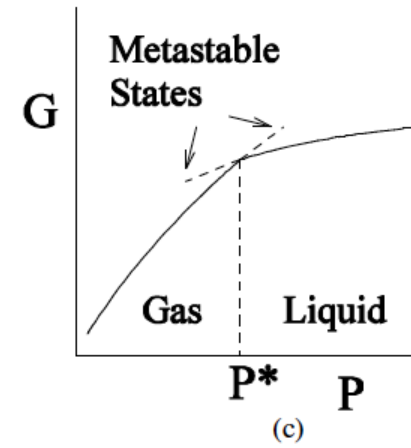
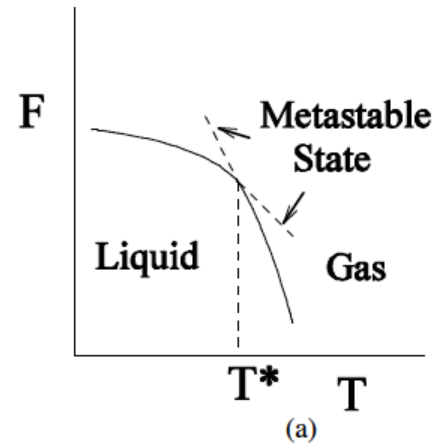
$$\oint_{P_{lg}} \frac{\partial G_N}{\partial P} dP = \oint_{P_{lg}} V dP = 0$$

The actual path in the P-V diagram is the line of constant pressure

Phase transition at constant Gibbs free energy

$$dG_l = dG_g$$

# Abrupt phase transition



# Clausius Clapeyron relation

Phase transition from liquid to vapor at a constant Gibbs free energy  $G(P, T, N)$

$$dG_l = dG_g$$

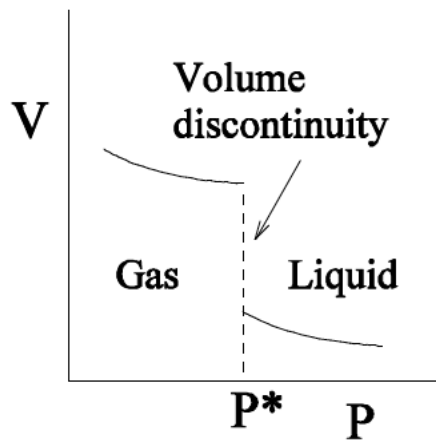
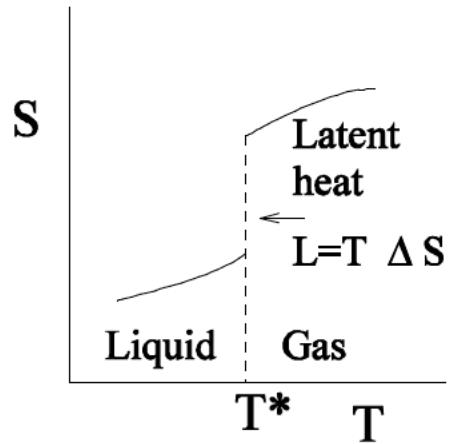
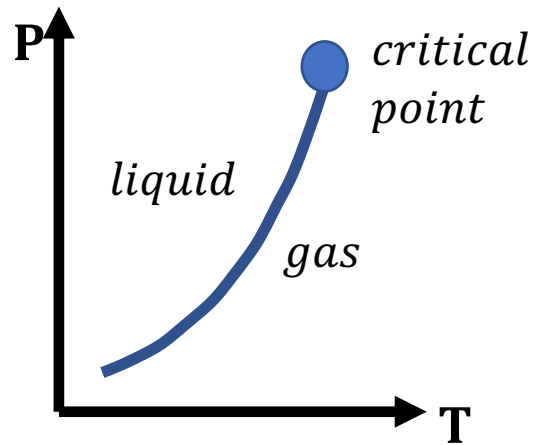
Clausius Clapeyron relation

$$-S_l dT + V_l dP = -S_g dT + V_g dP$$

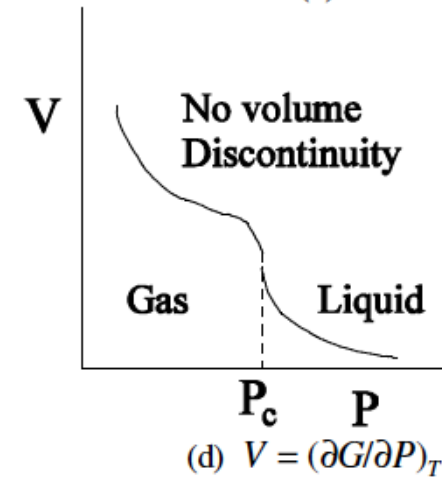
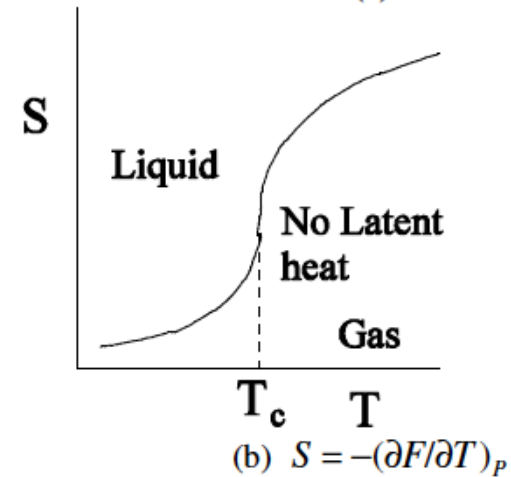
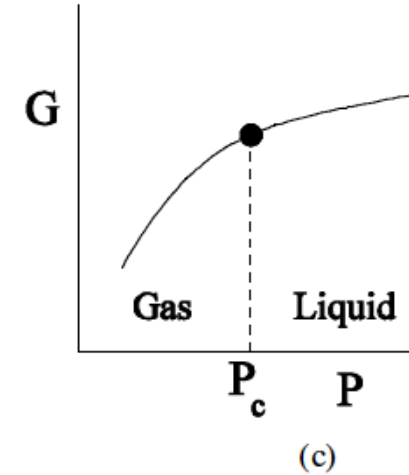
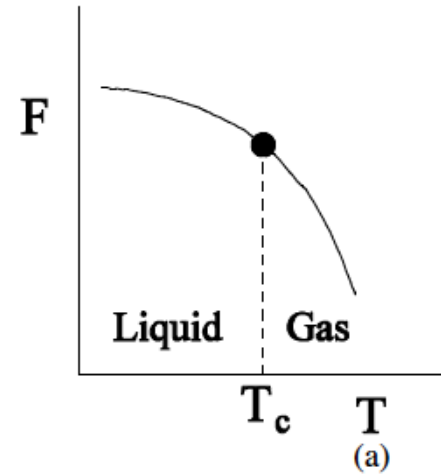
$$\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l} = \frac{\Delta S}{\Delta V} = \frac{L}{T \Delta V}, \text{ L is the latent heat of the phase transition}$$

- Entropy jumps going from a liquid to a gas  $S_g - S_l = \Delta \left( \frac{\partial G}{\partial T} \right)$
- Volume expansion going from a liquid to a gas  $V_g - V_l = \Delta \left( \frac{\partial G}{\partial P} \right)$

Clausius Clapeyron relation tells us how much the phase transition pressure changes with changing temperature



# Critical phase transition



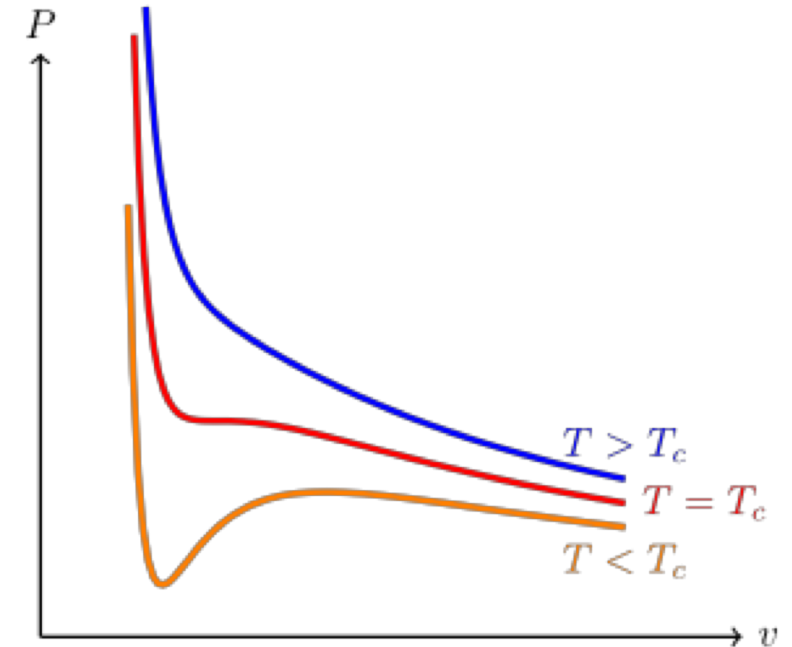
# Van der Waals fluids at the critical point $T_c$

Critical point defined as the inflection point of the isotherm in the  $P - V$  diagram:

$$\frac{\partial P}{\partial V} = 0, \quad \frac{\partial^2 P}{\partial V^2} = 0$$

*Applied to the van der Waals equation of state*

$$P_c = \frac{a}{27b^2}, \quad T_c = \frac{8a}{27bk}, \quad \rho_c = \frac{N}{V_c} = \frac{1}{3b}$$



# Van der Waals fluids near $T_c$

$$P = \frac{\rho kT}{1 - \rho b} - a\rho^2$$

Dimensionless equation of state

$$P_r = \frac{P}{P_c}, \quad T_r = \frac{T}{T_c}, \quad V_r = \frac{V}{V_c}$$

$$\left(P_r + \frac{3}{V_r^2}\right) \left(V_r - \frac{1}{3}\right) = \frac{8}{3} T_r$$

Isothermal compressibility

$$\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P} \sim |T - T_c|^{-\gamma}, \quad \gamma_{MF} = 1$$



# Van der Waals fluids near $T_c$

$$P = \frac{\rho kT}{1 - \rho b} - a\rho^2$$

Equation of state for relative fluctuations near the critical point

$$\Delta p = \frac{P}{P_c} - 1, \quad \Delta t = \frac{T}{T_c} - 1, \quad \Delta \rho = \frac{\rho}{\rho_c} - 1$$

$$\Delta p = (4 + 6\Delta\rho)\Delta t + \frac{3}{2}\Delta\rho^3$$

Critical exponents:

- $\Delta t = 0 \rightarrow \Delta p \approx \Delta\rho^\delta \rightarrow \left| \frac{P - P_c}{P_c} \right| \sim \left| \frac{\rho - \rho_c}{\rho_c} \right|^\delta$ ,  $\delta_{MF} = 3$
- $\Delta p = 0 \rightarrow \Delta\rho \approx \Delta t^\beta \rightarrow \left| \frac{\rho - \rho_c}{\rho_c} \right| \sim \left| \frac{T - T_c}{T_c} \right|^\beta$ ,  $\beta_{MF} = 1/2$

# Van der Waals fluids at the critical point

Internal energy:

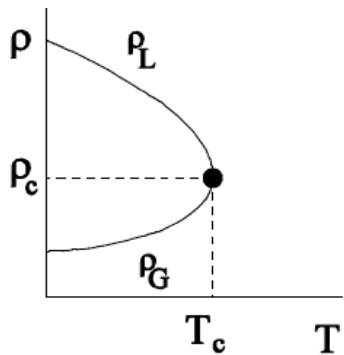
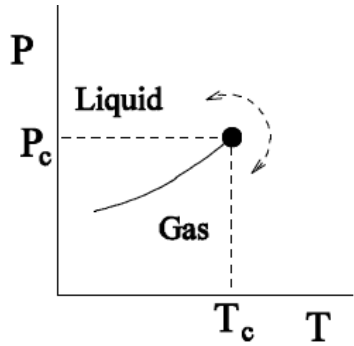
$$E = \langle H \rangle = \frac{3}{2}NkT + N\bar{u} = \frac{3}{2}NkT - \frac{aN^2}{V}$$

Heat capacity:

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = \frac{3}{2}Nk \sim (T - T_c)^\alpha, \quad \alpha_{MF} = 0$$

# Ising universality class in the mean-field

## Correspondence between magnetics and fluids at the critical point



Gas-Liquid	Magnets
Volume, $V$ or density, $\rho$	Mean magnetization, $-M$
Pressure, $P$	Magnetic field, $B$
Gibbs free energy, $G(P, T)$	Gibbs free energy, $G(B, T)$
Compressibility, $\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P}$	Susceptibility, $\chi = \frac{\partial M}{\partial B}$
Heat capacity, $C_P = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_P$	Heat capacity, $C_B = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_B$

Specific heat:

$$C_B \propto |T - T_c|^{-\alpha} \quad \alpha = 0$$

Order parameter:

$$M \propto (T_c - T)^\beta \quad \beta = 1/2$$

Susceptibility:

$$\chi \propto |T - T_c|^{-\gamma} \quad \gamma = 1$$

Critical isotherm:

$$B \propto |M|^\delta \quad \delta = 3$$

