

Lecture 14

01.03.2019

Phase transitions and summary of Module III

Classical gases and liquids

- Statistical mechanics of *weakly-interacting* classical *indistinguishable* particles
- Translational and rotational symmetric Hamiltonian H_N

$$H_N(p, q) = \sum_{j=1}^{3N} \frac{p_j^2}{2m} + U(q_1, q_2, \dots, q_{3N})$$

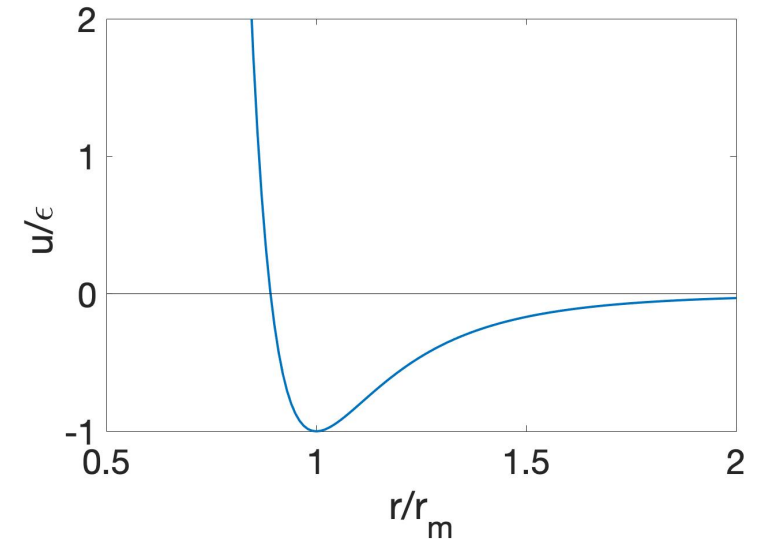
$$H_N = \sum_{i=1}^N \frac{|\vec{p}_i|^2}{2m} + \frac{1}{2} \sum_{j \neq i} u(r_{ij}), \quad r_{ij} = |\vec{r}_i - \vec{r}_j|, \quad \vec{r} = (x, y, z), \quad \vec{p} = (p_x, p_y, p_z)$$

- Homogeneous and isotropic matter: gases and liquids

- $Z_N(T, N) = \frac{1}{N!} \int d\omega e^{-\beta H_N(p, q)} = \frac{1}{N!} \frac{Q_N}{\Lambda^{3N}}$

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

configurational partition function: contains all the information about the particle positions



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 hard to compute

- 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

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

Self-consistent equation

$$\bar{u} = \frac{\langle U_N \rangle}{N} = \frac{\rho}{2} \int d\vec{r} u(r) g(r) = -\frac{Na}{V}, \quad a > 0$$

Mean-field approximation

Canonical partition function

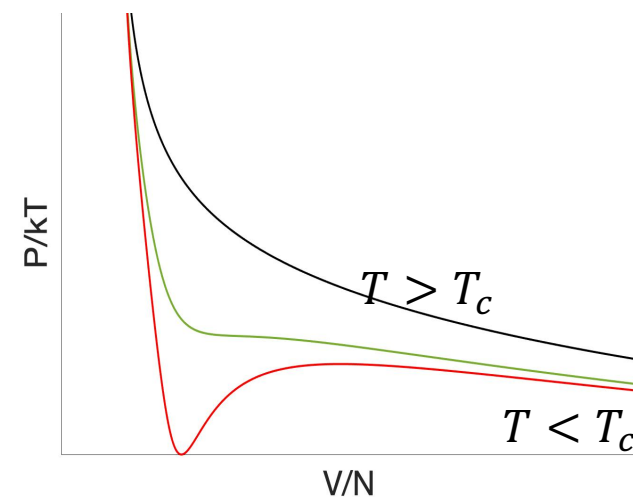
$$Z_N = \frac{1}{N!} \frac{Q_N}{\Lambda^{3N}}, \quad Q_N = (V - Nb)^N e^{-N\beta\bar{u}}$$

Helmholtz free energy

$$F_N = -kT \ln(Z_N)$$
$$F_N = -NkT \left[\ln \left(\frac{V}{N\Lambda^3(T)} \right) + 1 \right] - NkT \ln \left(1 - \frac{Nb}{V} \right) - \frac{N^2 a}{V}$$

Equation of state

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



Phase transition

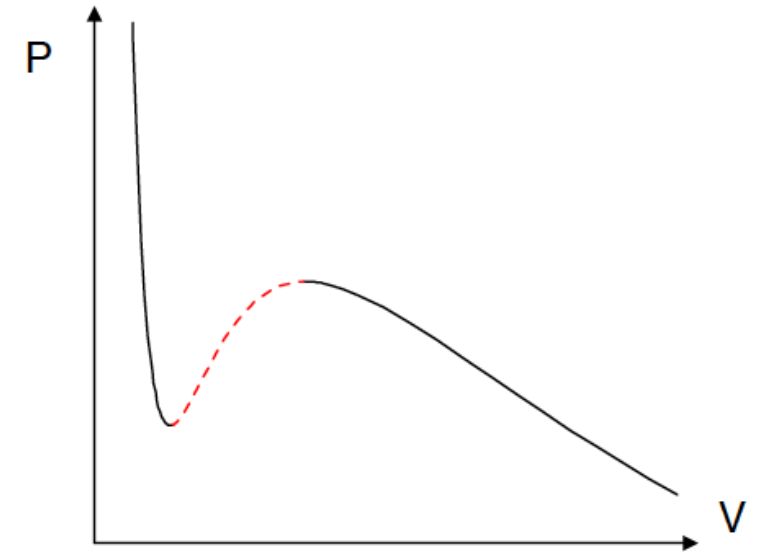
$$\frac{P}{kT} = \frac{N}{V - Nb} - \frac{a N^2}{kT V^2}$$

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

$$\frac{\partial P}{\partial V} = 0, \quad \frac{\partial^2 P}{\partial V^2} = 0 \rightarrow P_c = \frac{a}{27b^2}, \quad T_c = \frac{8a}{27bk}, \quad V_c = 3b$$

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

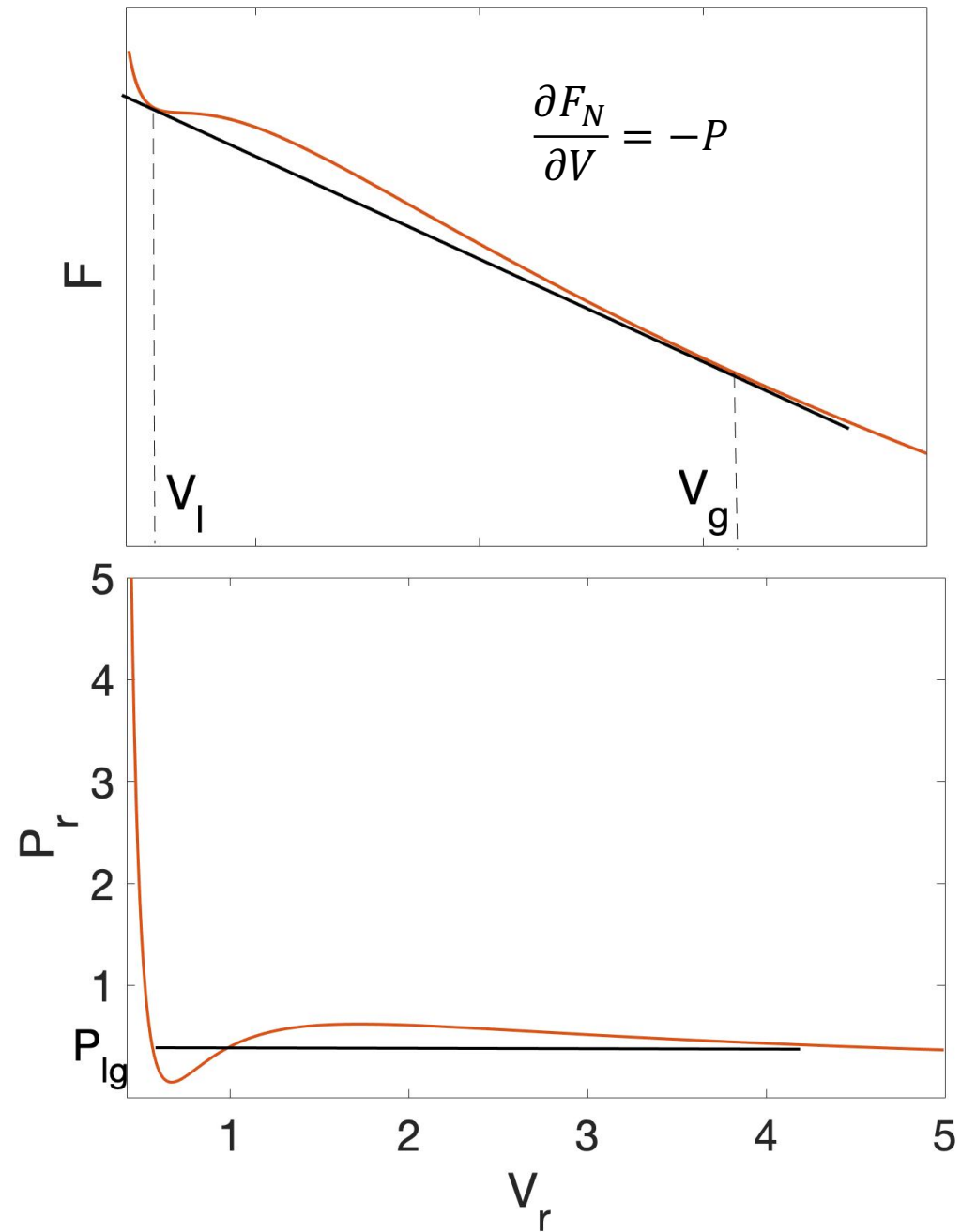
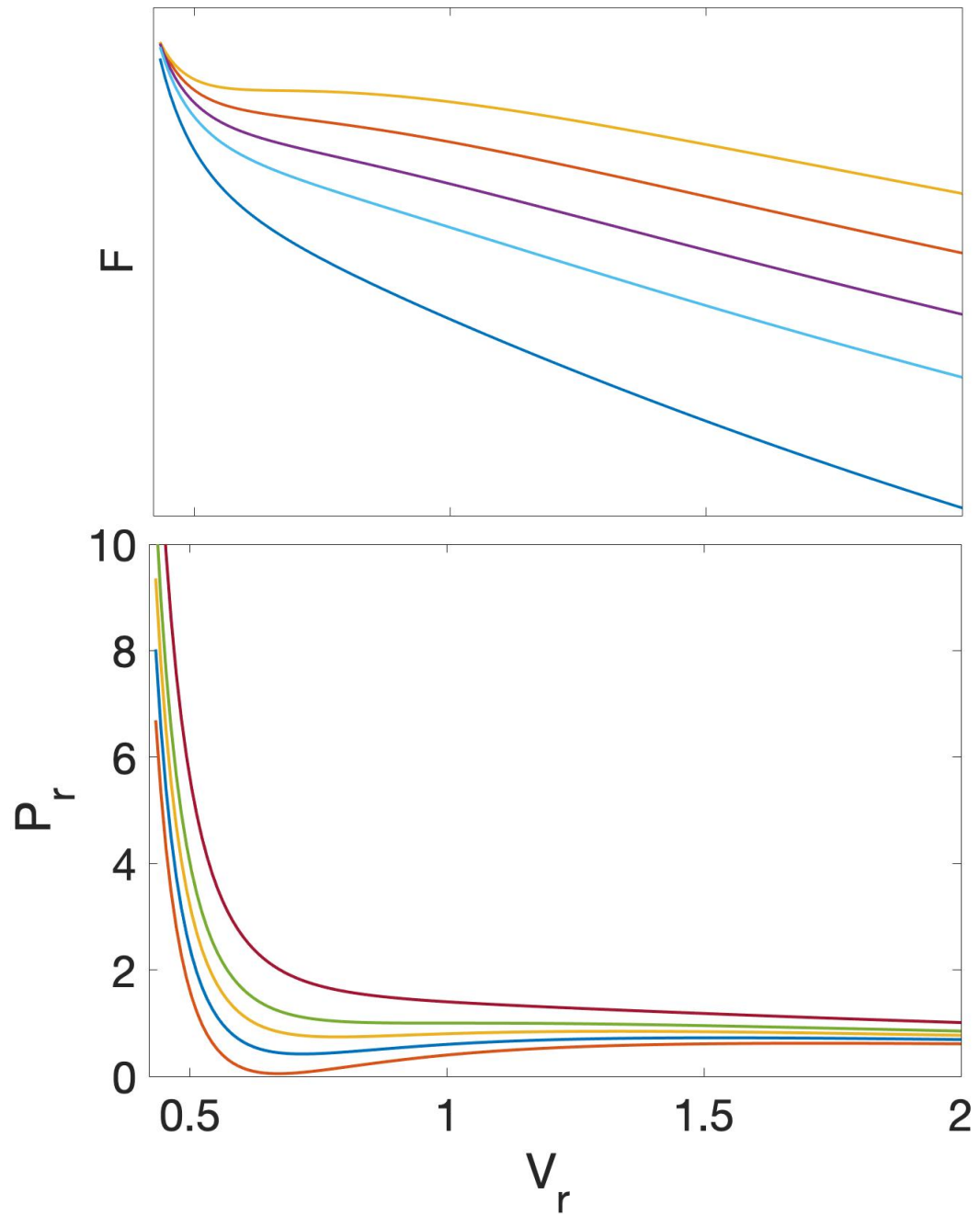
$$P_r = \frac{8 T_r}{3 V_r - 1} - \frac{3}{V_r^2}$$



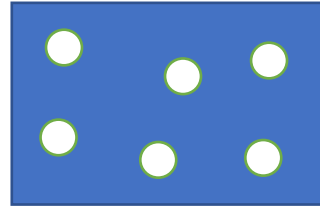
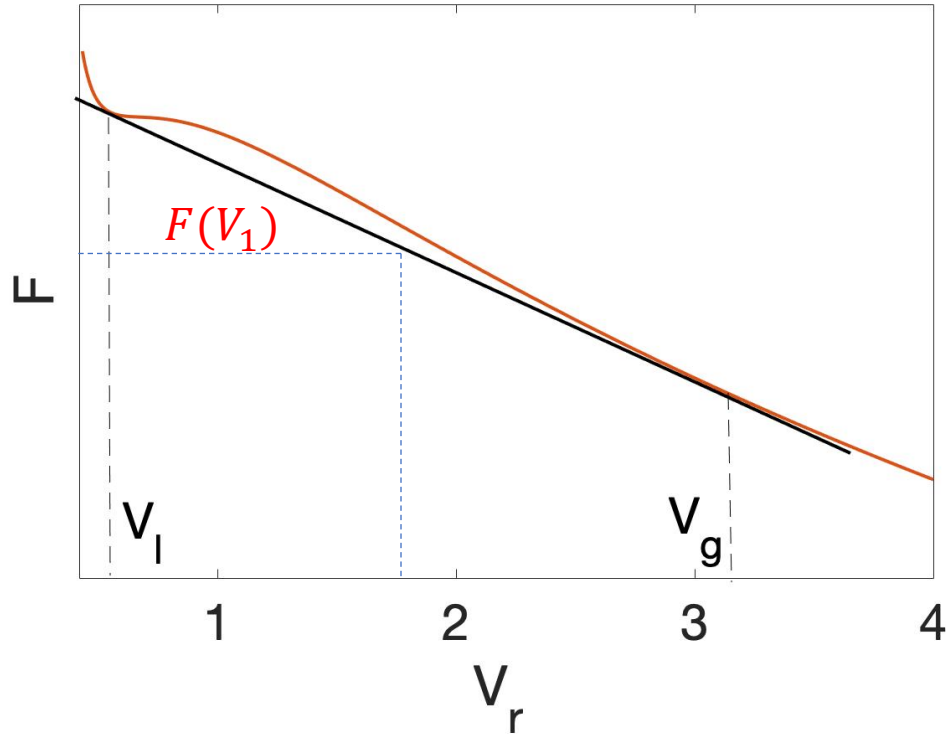
$P(V)$ curve becomes non-monotonic $\frac{\partial P}{\partial V} > 0$ is an unstable branch

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

$\kappa = -\frac{1}{V} \frac{\partial V}{\partial P} < 0$ compressibility is negative, sign that there is a thermodynamic instability



Abrupt phase transition $T < T_c$



Phase separation

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

Common tangent construction

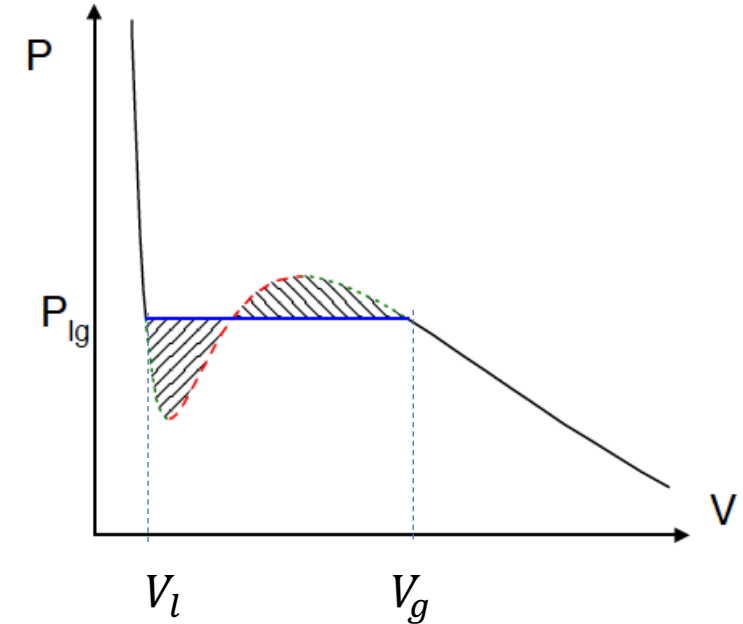
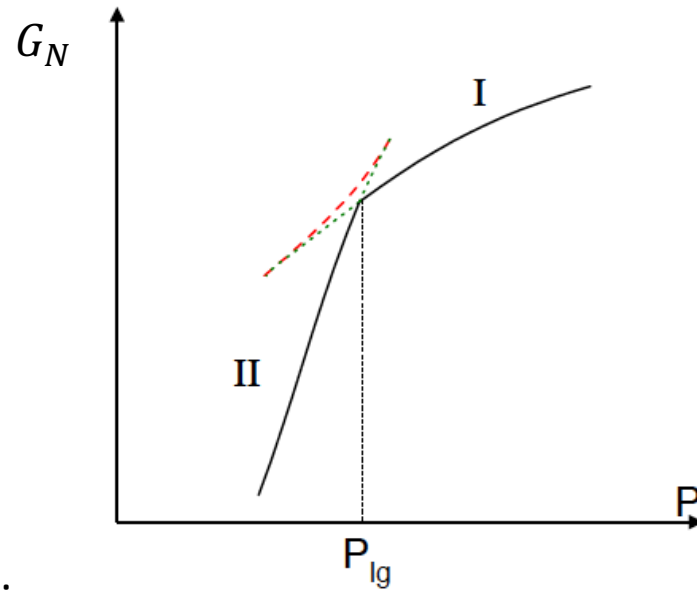
$$F_N(V_1) = \frac{N_l}{N} F_{N_l}(V_l) + \frac{N_g}{N} F_{N_g}(V_g)$$

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

In the coexistence region, the pressure is constant

$$P = - \left(\frac{\partial F_N}{\partial V} \right)_T = - \frac{F_{N_g}(V_g) - F_{N_l}(V_l)}{V_g - V_l} = P_{lg}$$

Fluid mixture below T_c



Maxwell equal-area construction:

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

$$\oint_{P_{lg}} \frac{\partial G_N}{\partial P} dP = \oint_{P_{lg}} V dP = 0 \rightarrow P_{lg} (V_g - V_l) = \int_{V_l}^{V_g} P(V) dV$$

Phase transition at constant Gibbs free energy

$$dG_l = dG_g$$

Clausius Clapeyron relation

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

$$dG_l = dG_g$$

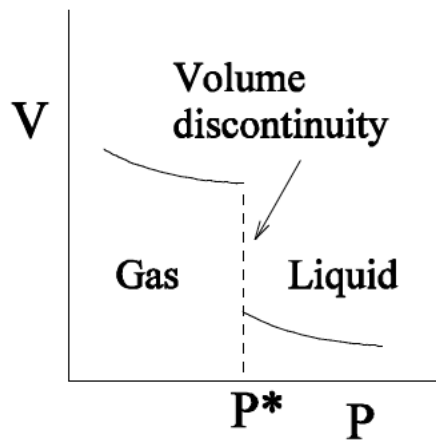
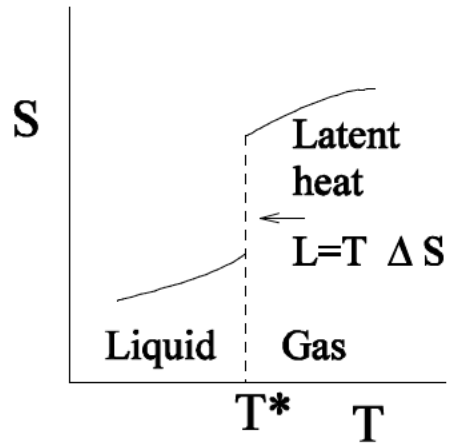
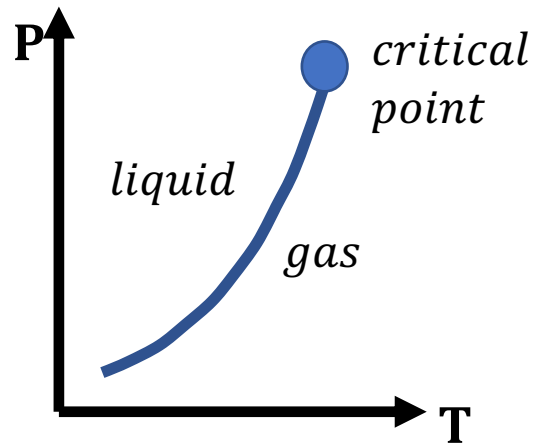
Clausius Clapeyron relation

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

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

- 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



Liquid-gas phase transitions

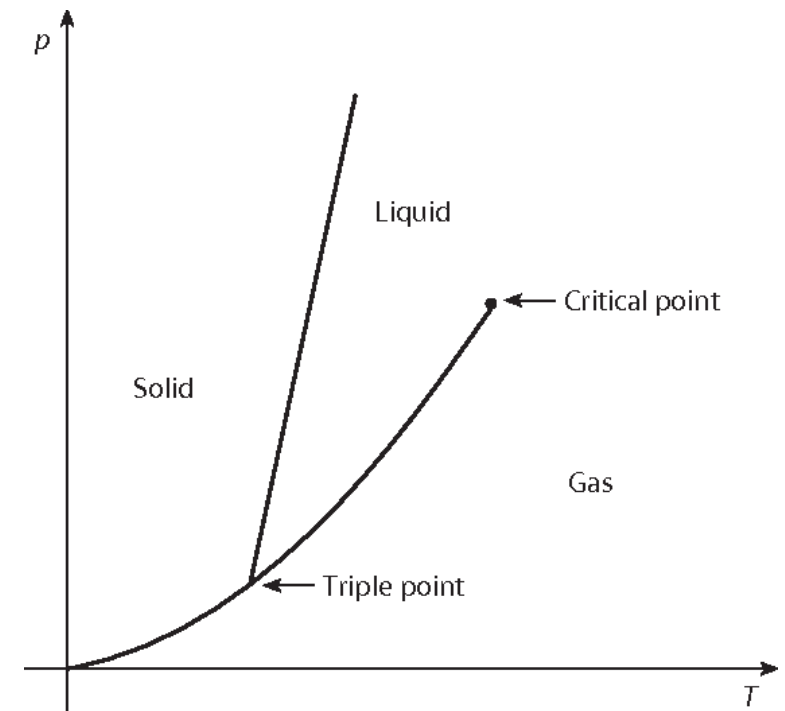
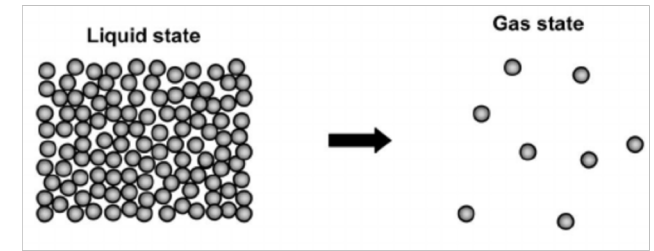
- Van der Waals equation of state for fluids

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$

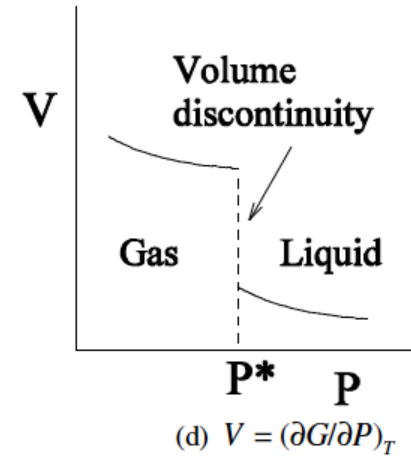
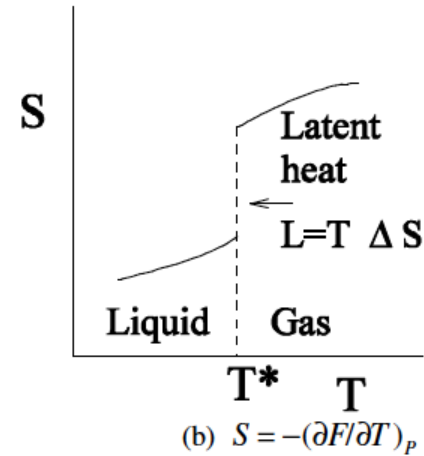
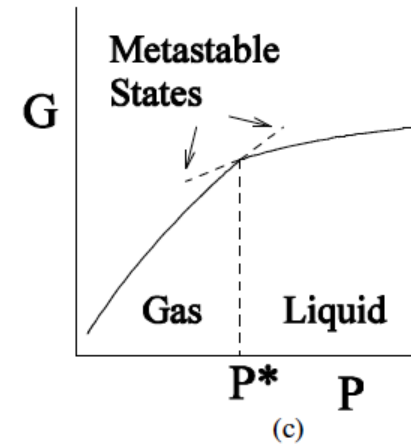
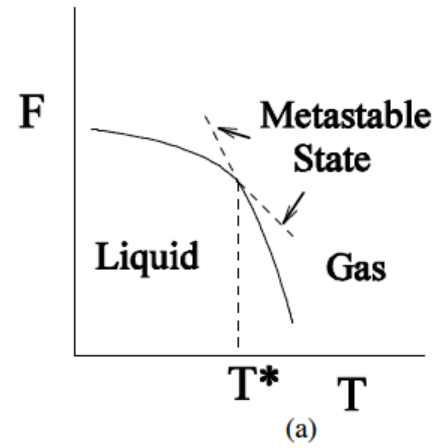
- Abrupt phase transition is represented by the phase coexistence boundary

$P_{lg}(T_{lg})$ in the P-T phase diagram

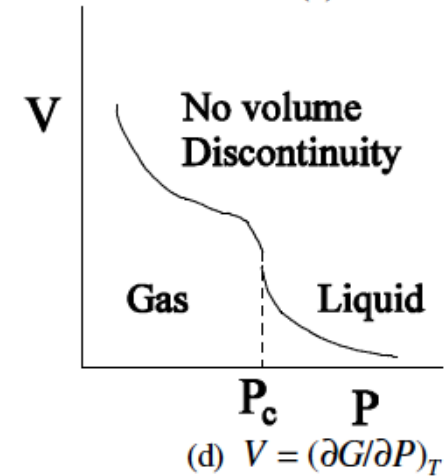
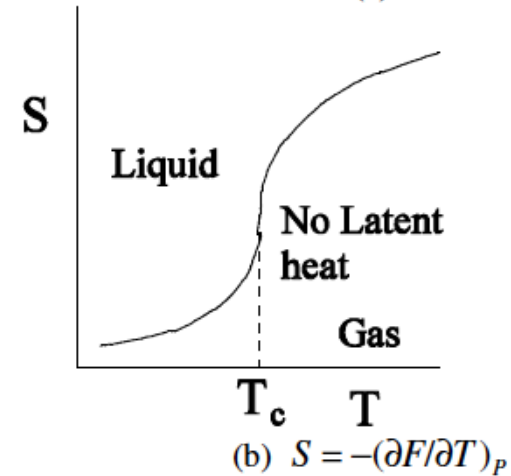
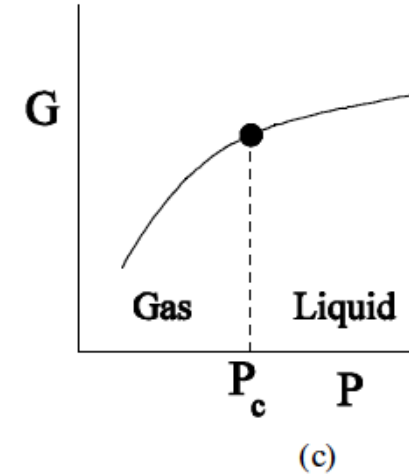
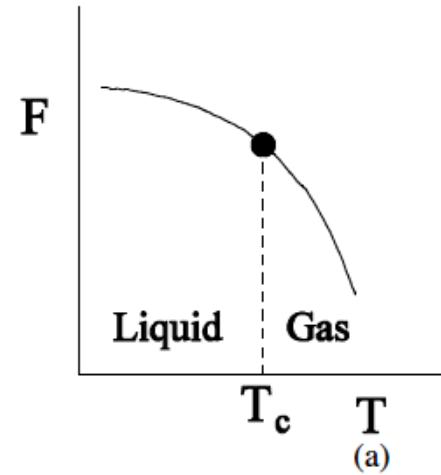
- **First order** derivatives of the thermodynamic potential are discontinuous: entropy and volume
- **Clausius Clapeyron relation:** How the pressure depends on the temperature on the vaporisation/condensation phase boundary
- Phase transition from liquid to vapor at a constant Gibbs free energy $G(P, T, N)$
- There is a **unique critical point** (T_c, P_c, V_c) at which the phase transition turns **critical**
 - First order derivatives of the thermodynamic potential are *continuous*, but the *second order* derivatives, like heat capacity, susceptibility, are *power-law divergent near the critical point*
 - *Critical phase transitions* are robust to microscopic details and exhibit *universal scaling* properties, e.g. **critical scaling exponents**



Abrupt phase transition



Critical phase transition



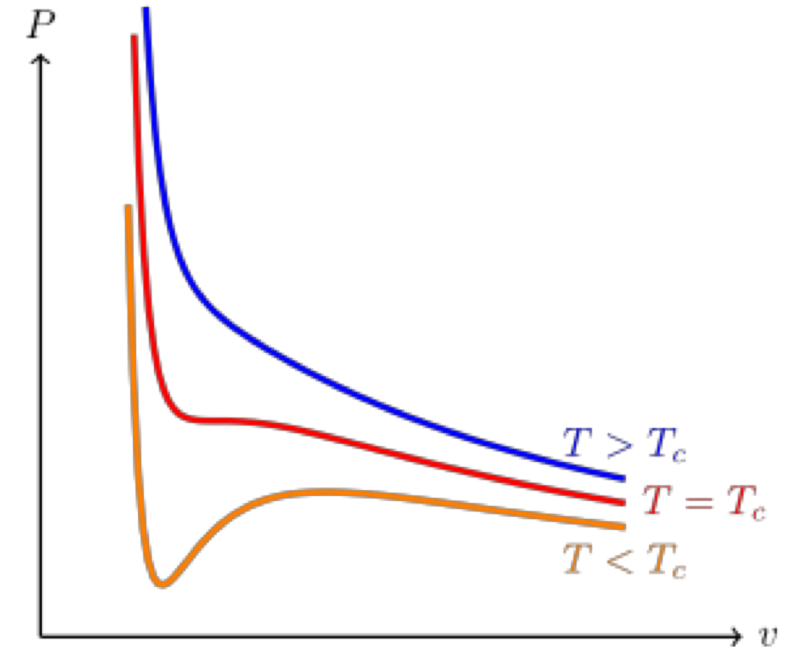
Van der Waals fluids at the critical point T_c

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:

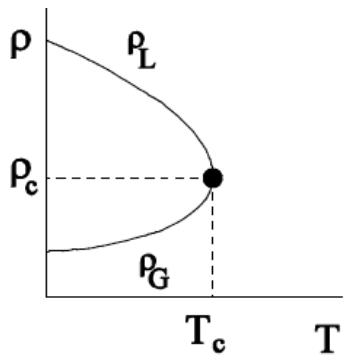
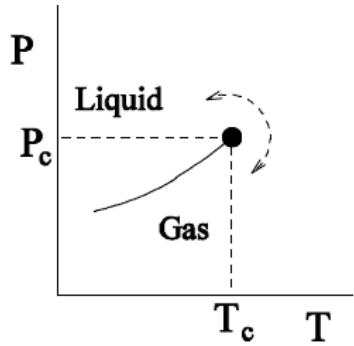
$$E = \langle H \rangle = \frac{3}{2}NkT + N\bar{u} = \frac{3}{2}NkT - \frac{aN^2}{V}$$

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, ρ	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:

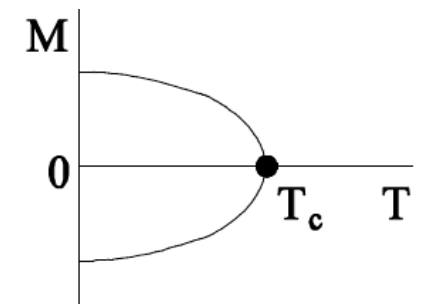
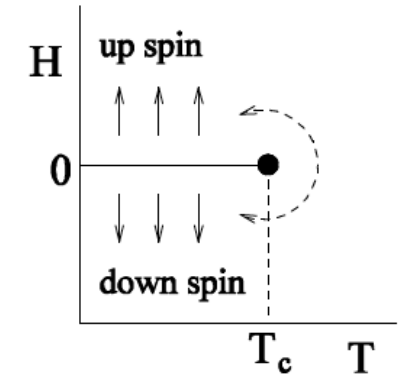
$$M \propto (T_c - T)^\beta \quad \beta = 1/2$$

Susceptibility:

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

Critical isotherm:

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



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:**

- We construct an hierarchy of reduced particle configurations (clusters expansion) in which we fix few particle positions and integrate out the remaining spatial coordinates

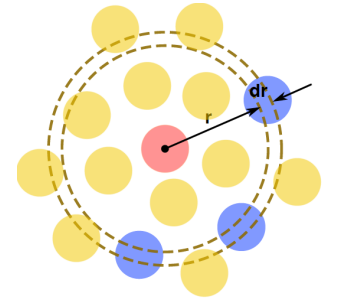


- We construct the first two terms in the cluster expansion: mean particle density and pair-correlation function
- Thermodynamic properties, like *pressure*, *internal energy*, can be expressed in terms of these reduced probabilities

Correlation functions

Mean density of particles is uniform for a *translational and isotropic system*

$$\langle n(\vec{r}) \rangle = \left\langle \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) \right\rangle = \rho = \frac{N}{V}$$



Density correlation of pairs of particles separated by $\vec{r} - \vec{r}'$

$$\langle n(\vec{r})n(\vec{r}') \rangle = \left\langle \sum_{i=1}^N \sum_{j=1}^N \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) \right\rangle \equiv G(\vec{r} - \vec{r}')$$

$$G(\vec{r} - \vec{r}') = \rho^2 g(\vec{r} - \vec{r}') + \rho \delta(\vec{r} - \vec{r}'),$$
$$\rho^2 g(\vec{r} - \vec{r}') \equiv \rho^2 g(|\vec{r} - \vec{r}'|) = \rho^2 g(r)$$

Average properties

Average energy

$$\langle E \rangle = \frac{3N}{2} kT + \frac{\rho N}{2} \int d\vec{r} u(r) g(r)$$

Particle number fluctuations

$$\langle \Delta N^2 \rangle = \langle N \rangle + \langle N \rangle \rho \int d\vec{r} [g(r) - 1]$$

Virial theorem

$$2\langle K \rangle = - \left\langle \sum_k \vec{r}_k \cdot \vec{F}_k \right\rangle \rightarrow 3NkT = \frac{N\rho}{2} \int d\vec{r} r^2 u'(r) g(r) + 3PV$$

$$P = \rho \left[kT - \frac{\rho}{6} \int d\vec{r} r u'(r) g(r) \right]$$