PHYS 10352

PART I: CLASSICAL THERMODYNAMICS

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WEEK 6: PHASE CHANGES

RECAP

▶ Starting from the <u>fundamental thermodynamic relation</u> we can derive the thermodynamic potentials:

$$F(T, V) = E - TS$$

$$G(T, P) = E - TS + PV$$

$$H(S, P) = E + PV$$

▶ Helmholtz free energy, F, is decreasing for spontaneous processes at constant temperature and volume.
▶ Gibbs free energy, G, determines the direction of spontaneous processes at constant pressure and temperature.
▶ The <u>second derivatives</u> of the thermodynamic potentials give us the Maxwell relations:
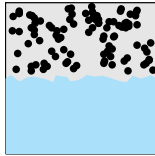
$$\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$
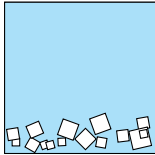
$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$$

PHASE EQUILIBRIUM

T & *V*
fixed

Liquid-Gas coexistence

$P = 1$ atm.
$T = 273.15$ K

Solid-Liquid coexistence

We can find the conditions for phase equilibrium by considering the total, isolated system to be composed of two open systems:

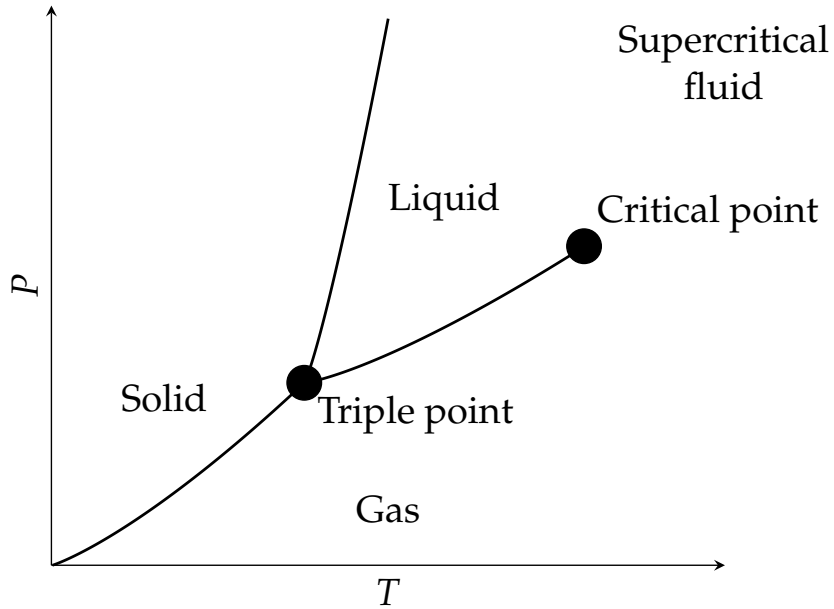$$S(E, V, N) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2),$$

PHASE EQUILIBRIUM

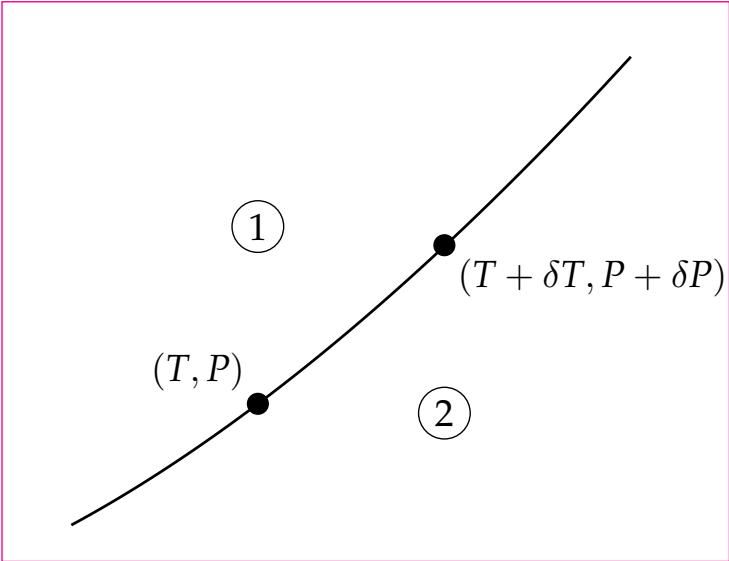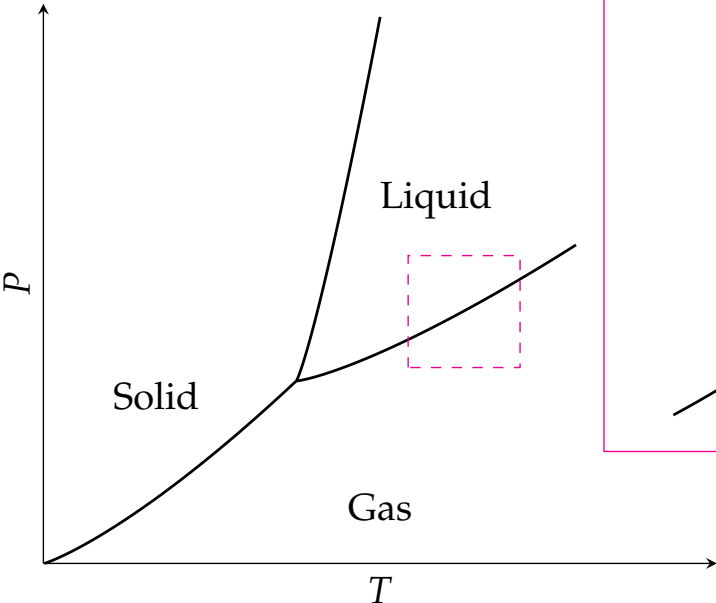As the overall system is isolated, it reaches equilibrium when entropy is maximised; $dS = 0$, i.e.:

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN = 0.$$

- $T_1 = T_2$, no heat flow between the systems.
- $P_1 = P_2$, the systems are at mechanical equilibrium.
- $\mu_1 = \mu_2$, there is no preference to be in one state over the other.

PHASE EQUILIBRIUM

PHASE EQUILIBRIUM

PHASE EQUILIBRIUM
CLAUSIUS-CLAPEYRON EQUATION

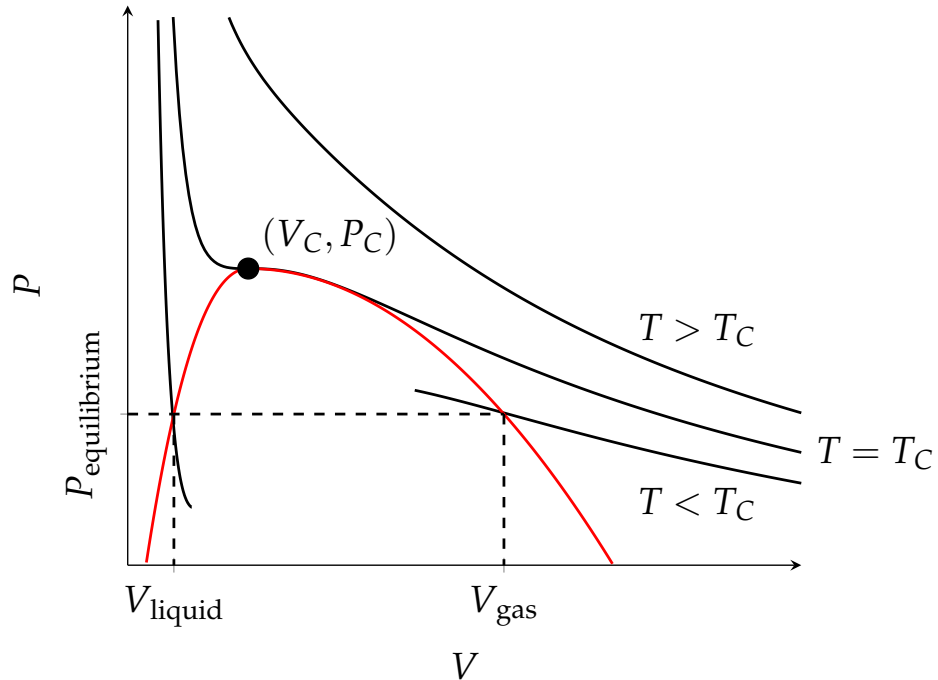The Clausius-Clapeyron relation relates different points of phase coexistence.

(For instance, how the boiling point of water changes with pressure, e.g. at different altitudes.)

$$\frac{dP}{dT} = \frac{\Delta S^m}{\Delta V^m} = \frac{\Delta H^m}{T \Delta V^m}$$

where S^m and V^m refer the to entropy and volume per mole, respectively, and H^m is the enthalpy per mole, also referred to as *the latent heat of transformation*.
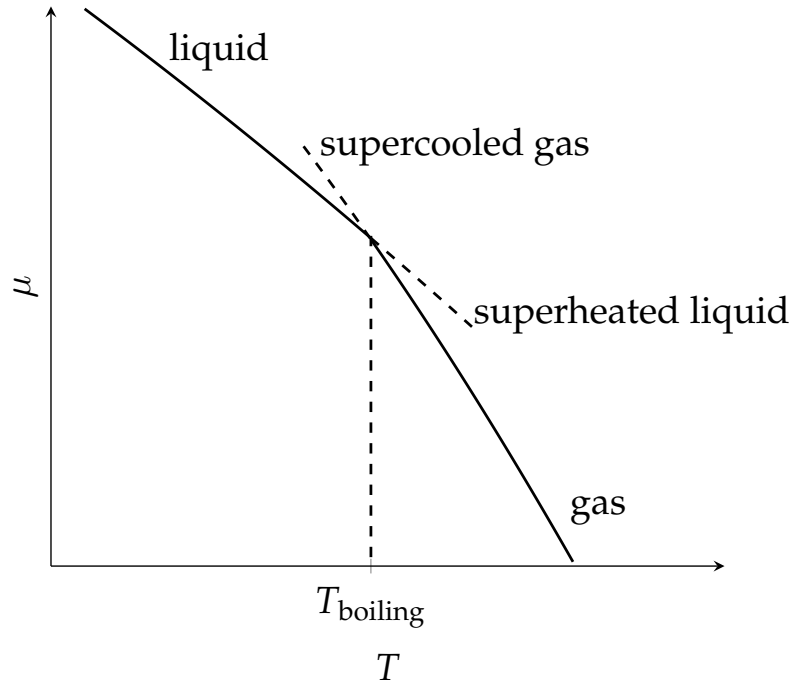
REAL GASES
VAN DER WAALS EQUATION

$$P = \frac{nRT}{V - nb} - a\frac{n^2}{V^2}$$

The Van der Waals equation is cubic for V:

$$PV^2(V - nb) - nRTV^2 + an^2(V - nb) = 0,$$

therefore there are either one real root or three. We find this is dependent on the temperature:

- For $T > T_C = \frac{8a}{27bR}$, there is only one solution for V where P decreases with V.
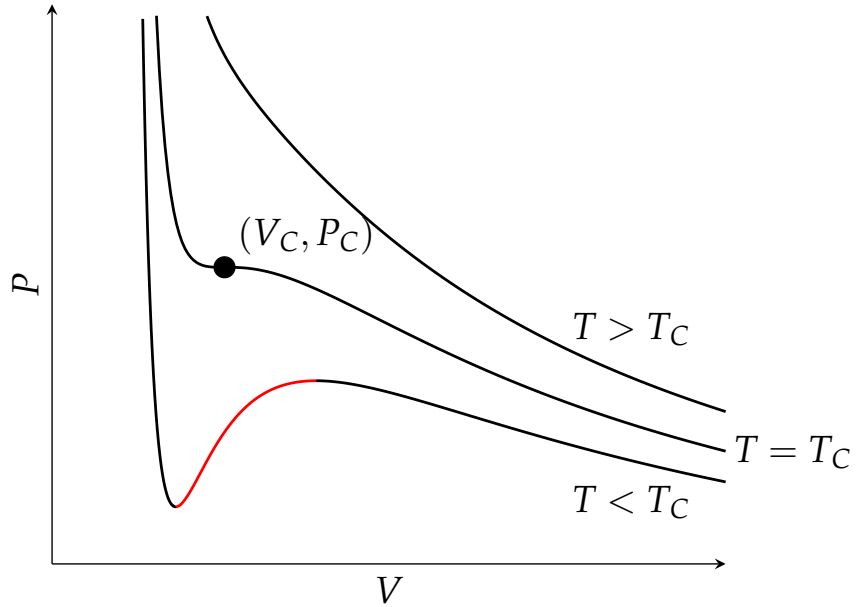- For $T = T_C$, the isotherm has a point of inflexion where

$$\left(\frac{\partial P}{\partial V}\right)_{T_C} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_C} = 0 \tag{1}$$

  at $V_C = 3nb$.
- For $T < T_C$ there are three solutions, however one is unphysical where $\left(\frac{\partial P}{\partial V}\right)_{T_C} > 0$.

SUMMARY

▶ Points of phase equilibrium, i.e. co-existence, are described by the Clausius-Clapeyron Equation:

$$\frac{dP}{dT} = \frac{\Delta S^m}{\Delta V^m} = \frac{\Delta H^m}{T \Delta V^m}$$

▶ The **triple point** describes the state at which three phases can co-exist.

▶ The **critical point** described the point beyond which liquid and gas cannot be distinguished.

▶ The equation of state for real gases is approximated by the Van der Waals Equation:

$$P = \frac{nRT}{V - nb} - a\frac{n^2}{V^2}$$

▶ The VdW equation can be solved to find the state variables (T_C, V_C, P_C) at the triple point.