Classification of phase transitions [tln28]

Consider a 1-component fluid system with phases I and II.

The Gibbs free energy has a different functional dependence on its natural variables in the two phases:

$$G^I(T,p,n) = \mu^I(T,p)n, \quad G^{II}(T,p,n) = \mu^{II}(T,p)n.$$

For given values of T and p, the equilibrium state is the one with the lowest Gibbs free energy, i.e the state with the lower chemical potential.

At the transition: $G^I = G^{II}$, i.e. $G^* = \mu^*(n^I + n^{II})$ with $n^I + n^{II} = n$.

Discontinuous transition:

The volume and the entropy change discontinuously:

1. $\left(\frac{\partial G}{\partial n}\right)_{T,p}^{I} = \left(\frac{\partial G}{\partial n}\right)_{T,p}^{II} \Rightarrow \mu^I = \mu^{II} = \mu^*.$
2. $\left(\frac{\partial G}{\partial p}\right)_{T,n}^{I} \neq \left(\frac{\partial G}{\partial p}\right)_{T,n}^{II} \Rightarrow V^I \neq V^{II}.$
3. $\left(\frac{\partial G}{\partial T}\right)_{n,p}^{I} \neq \left(\frac{\partial G}{\partial T}\right)_{n,p}^{II} \Rightarrow S^I \neq S^{II}.$

Latent heat (change in enthalpy): $\Delta E = \Delta(G + TS) = T\Delta S$

Continuous transition:

The volume and the entropy change continuously. Discontinuities or divergences occur in higher-order derivatives.

1. $\left(\frac{\partial G}{\partial n}\right)_{T,p}^{I} = \left(\frac{\partial G}{\partial n}\right)_{T,p}^{II} \Rightarrow \mu^I = \mu^{II} = \mu^*.$
2. $\left(\frac{\partial G}{\partial p}\right)_{T,n}^{I} = \left(\frac{\partial G}{\partial p}\right)_{T,n}^{II} \Rightarrow V^I = V^{II}.$
3. $\left(\frac{\partial G}{\partial T}\right)_{n,p}^{I} = \left(\frac{\partial G}{\partial T}\right)_{n,p}^{II} \Rightarrow S^I = S^{II}.$