1 Equilibrium between Phases

vapor $\rightleftharpoons$ water $\rightleftharpoons$ ice

General Aspects :

- For an isolated system, at equilibrium, the entropy is maximized
- For multiple systems, we must consider the entire system's entropy as a maximized quantity.

Case 1: Isolated System

$$Q = \Delta\bar{E} + W$$
$$W = 0, Q = 0, \Delta\bar{E} = 0$$

For some fluctuation:

$$P(y) \propto \Omega(y) = e^{S(y)/k}, \quad \frac{P(y)}{P(\tilde{y})} = \frac{e^{S(y)/k}}{e^{S(\tilde{y})/k}} = e^{\Delta S/k}$$

where the relative prob is exponentially suppressed.

Case 2: System is in contact with a reservoir at T

$$A' + A = A^{(0)}$$

where $S^{(0)}$ is maximized

$$\Delta S^{(0)} \geq 0 = \Delta S + \Delta S'$$

Heat transfer from the heat reservoir A' (which doesn't change in Tempertature) to the system A is

$$\Delta S' = -\frac{Q}{T_0}$$

In additiion, there is no work done on the system i.e. $Q = \Delta\bar{E}$ so

$$\Delta S^{(0)} = \Delta S - \frac{Q}{T_0} = \frac{T_0\Delta S - \Delta\bar{E}}{T_0} = \frac{\Delta(T_0 S - \bar{E})}{T_0} = \frac{-F_0}{T_0}$$

where

$$F_0 = T_0 S - \bar{E}$$

is the Helmholtz free energy of system A as it has the same temperature of the reservoir. Furthermore,

$$\Delta F_0 \leq 0$$

So the equilibrium condition requires a minimized free energy!