# Chapter 2

Consider a multiphase, multi-component system

$$E = \sum_{\alpha=1}^{\nu} E^{(\alpha)}, \quad \nu = \#\ phases$$

Different phases = different subsystems

$$S = \sum_{\alpha=1}^{\nu} S^{(\alpha)}$$

$$V = \sum_{\alpha=1}^{\nu} V^{(\alpha)}$$

$$n_i = \sum_{\alpha=1}^{\nu} n_i^{(\alpha)}$$ , $n_i^{(\alpha)}$ = # of moles of species *i* in phase $\alpha$

$$\delta E = \sum_{\alpha=1}^{\nu} T^{(\alpha)} \delta S^{(\alpha)} - p^{(\alpha)} \delta V^{(\alpha)} + \sum_{i=1}^{r} \mu_i^{(\alpha)} \delta n_i^{(\alpha)}$$

*r* = # species

At equilibrium

$$(\delta E)_{S,V,n_i} \geq 0$$

$$\sum \delta S^{(\alpha)} = 0$$

$$\sum \delta V^{(\alpha)} = 0$$

$$\sum \delta n_i^{(\alpha)} = 0, \quad i = 1, 2, \ldots, r$$

This follows from the fact the total S, V, n are constant

Special case $\nu = 2$

$$\delta S^{(1)} = -\delta S^{(2)}$$

$$\delta V^{(1)} = -\delta V^{(2)}$$

$$\delta n_j^{(1)} = -\delta n_j^{(2)}$$

$$\delta E = \left(T^{(1)} - T^{(2)}\right)\delta S^{(1)} - \left(p^{(1)} - p^{(2)}\right)\delta V^{(1)} + \sum_{i=1}^{r}\left(\mu_i^{(1)} - \mu_i^{(2)}\right)\delta n_i^{(1)}$$

Must hold for all small unconstrained variations $\delta S^{(1)},\ \delta V^{(1)},\ \delta n_i^{(1)}$

and since $\delta E \geq 0$

$$\Rightarrow T^{(1)} = T^{(2)},\ p^{(1)} = p^{(2)}, \mu_i^{(1)} = \mu_i^{(2)}$$

which implies $\left(\delta E\right)_{S,V,n_i} = 0$

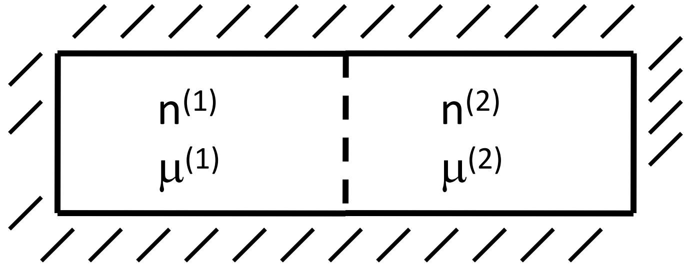
for small displacements away from equilibrium

Mass equilibrium: $\mu^{(1)} = \mu^{(2)}$

If $\mu^{(1)} > \mu^{(2)}$

mass will flow until equil. is achieved

$$\mu_{fin}^{(1)} = \mu_{fin}^{(2)}$$




$$\Delta S > 0$$

Assume no work done and no heat flow

$$\Delta S = -\frac{\mu^{(1)}}{T}\Delta n^{(1)} - \frac{\mu^{(2)}}{T}\Delta n^{(2)} = -\frac{\mu^{(1)} - \mu^{(2)}}{T}\Delta n^{(1)}$$

$$\Delta S > 0 \Rightarrow \Delta n^{(1)} < 0$$

matter flows from high $\mu$ to low $\mu$

gradients in $\frac{\mu}{T} \rightarrow$ mass flow

gradients in $\frac{1}{T} \rightarrow$ force causing heat flow

gradients in $\frac{P}{T} \rightarrow$ volume change

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$(\Delta E)_{S,V,n} > 0$ for displacements away from equilibrium

if unconstrained $(\delta E)_{X,V,n} = 0$

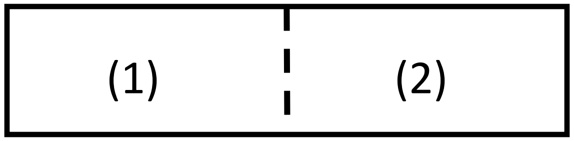
$$(\Delta E)_{S,V,n} = (\delta^2 E)_{S,V,n} + (\delta^3 E)_{S,V,n} + \ldots$$ near equilibrium

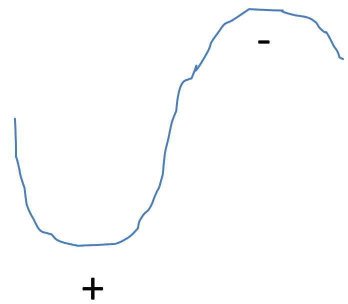
$$\left(\delta^{(2)} E\right)_{S,V,n} \geq 0$$

$\left(\delta^{(2)} E\right)_{S,V,n} > 0 \Rightarrow$ Stable wrt small fluctuations away from equilibrium

$\left(\delta^{(2)} E\right)_{S,V,n} = 0 \Rightarrow$ need to examine higher order variations

$$\left(\delta^{(2)}E\right)_{S,V,n} < 0 \Rightarrow$$ system is unstable wrt fluctuations




Consider the situation

$$\begin{cases} \delta S = 0 = \delta S^{(1)} + \delta S^{(2)} \\ \delta V^{(1)} = \delta V^{(2)} = 0 \\ \delta n^{(1)} = \delta n^{(2)} = 0 \end{cases}$$

$$\delta^2 E = \left(\delta^2 E\right)^{(1)} + \left(\delta^2 E\right)^{(2)} = \frac{1}{2}\left(\frac{\partial^2 E}{\partial^2 S}\right)_{V,n}^{(1)} \left(\delta S^{(1)}\right)^2 + \frac{1}{2}\left(\frac{\partial^2 E}{\partial S^2}\right)_{V,n}^{(2)} \left(\delta S^{(2)}\right)^2$$

$$\delta^2 E = \frac{1}{2}\left\{\left(\frac{\partial^2 E}{\partial S^2}\right)_{V,n}^{(1)} + \left(\frac{\partial^2 E}{\delta S^2}\right)_{V.n}^{(2)}\right\}\left[\delta S^{(1)}\right]^2$$

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_{V,n} = \left(\frac{\partial T}{\partial S}\right)_{V,n} = \frac{T}{C_V}$$

$$\left(\delta^2 E\right)_{S,V,n} = \frac{1}{2}\left\{\frac{T^{(1)}}{C_V^{(1)}} + \frac{T^{(2)}}{C_V^{(2)}}\right\}\left(\delta S^{(1)}\right)^2$$

$$= \frac{\left(\delta S^{(1)}\right)^2}{2} T\left[\frac{1}{C_V^{(1)}} + \frac{1}{C_V^{(2)}}\right]$$

$$\left(\delta^{(2)} E\right)_{S,V,n} \geq 0 \quad \Rightarrow \quad T\left[\frac{1}{C_V^{(1)}} + \frac{1}{C_V^{(2)}}\right] \geq 0$$

this should hold for any subdivision

$\Rightarrow C_V \geq 0$ | this is essential if the system is stable