PHYS 414: 4-3-20

$$-T(t)\,\dot{S}^i = \dot{\bar{E}} - T(t)\,\dot{S} + \sum_{\nu=1}^{L} f_\nu(t)\,\dot{\bar{x}}_\nu$$

goal: make right-hand side look like $\dot{\Psi}$ for some potential Ψ

$2L+3$ terms: $\bar{E}$

$T(t)$, S

$f_\nu(t)$, $\bar{x}_\nu$ $\quad \nu = 1, \ldots, L$

Claim: to accomplish this, we are going to constrain the sys so that $L+1$ quantities are fixed in time: either f_ν or $\bar{x}_\nu$ for each work term + then one more from either $\bar{E}$, T, or S

we will show that $\Psi(t) \xrightarrow[t\to\infty]{} \Psi^{eq}(\underbrace{\alpha_1, \ldots, \alpha_{L+1}}_{\text{fixed quantities}})$

min. value in equil.

concrete example: one work term $\dot{W} = P(t)\,\dot{\bar{V}}$

$$-T(t)\,\dot{S}^i = \dot{\bar{E}} - T(t)\,\dot{S} + P(t)\,\dot{\bar{V}}$$

$L=1$
fix 2 quantities

i) fix T, P: $\quad T(t) = T, \quad P(t) = P$

$$\underbrace{-T\dot{S}^i}_{\leq 0} = \dot{\bar{E}} - T\dot{S} + P\dot{\bar{V}}$$

$$= \frac{d}{dt}\underbrace{(\bar{E} - TS + P\bar{V})}_{\equiv G(t)}$$

$= 0$ only in equil.

$\equiv G(t)$ Gibbs free energy

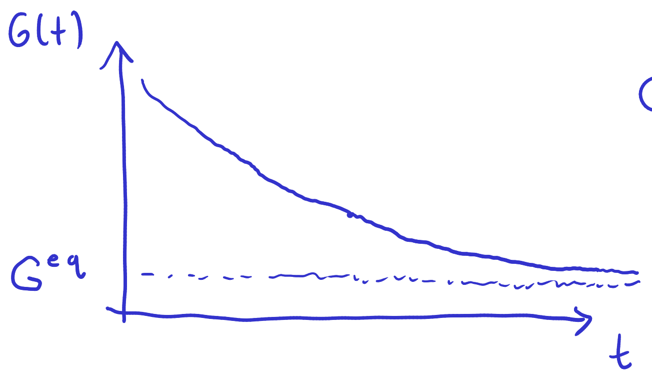
work in trans. from $m \to n$ $= P(V_n - V_m)$

$$S = -k_B \sum_n p_n \ln p_n$$

$\rightarrow 0$ min, $\rightarrow k_B \ln N$ max

$$\mathring{W} = \frac{1}{2} \sum_{nm} J_{nm} P (V_n - V_m)$$

$$= P \mathring{\bar{V}} \quad \text{valid instantaneously}$$



$$G(t) = \bar{E} - TS + P\bar{V}$$

$\bar{E}$: bounded from below by lowest energy state

$-TS$: bounded from below by $-Tk_B \ln N$

$P\bar{V}$: " " by smallest volume state

$$\boxed{\underbrace{G(t)}_{} \xrightarrow[t\to\infty]{} \underbrace{G^{eq}(T, P)}_{}}$$

Gibbs free energy is minimized if we fix T + P

ii) fix $T, \bar{V}$: $\quad T(t) = T, \quad \mathring{\bar{V}} = 0$

$$\Rightarrow -T\mathring{S}^i = \mathring{\bar{E}} - T\mathring{S}$$

$$= \frac{d}{dt} \underbrace{(\bar{E} - TS)}_{\equiv F(t)}$$

$\equiv F(t)$ Helmholtz free energy

$$\boxed{F(t) \xrightarrow[t\to\infty]{} F^{eq}(T, \bar{V})}$$

iii) fix S, P: $\quad \mathring{S} = 0, \quad P(t) = P$

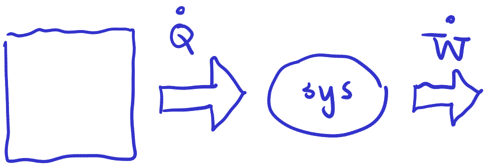
$$-T\mathring{S}^i = \mathring{\bar{E}} + P\mathring{\bar{V}}$$

$$= \frac{d}{dt} \underbrace{(\bar{E} + P\bar{V})}_{\equiv H(t)} = \mathring{H}$$

$\equiv H(t)$ enthalpy

$$\boxed{H(t) \xrightarrow[t\to\infty]{} H^{eq}(S, \bar{P})}$$

note: $\dot{H} = \dot{\bar{E}} + \bar{P}\dot{\bar{V}} = \dot{\bar{E}} + \dot{\bar{W}} = \dot{Q}$



if you want $\dot{H}$ to be zero (in equil.) $\Rightarrow$ need $\dot{Q} = 0$

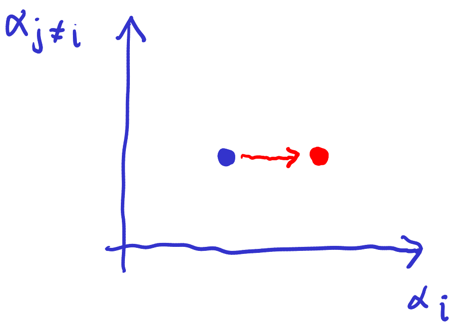
(thermally isolate sys, not allowing heat flow)

iv) fix $S, \bar{V}$: $\quad -T\dot{S}^i = \dot{\bar{E}} = \frac{d}{dt}\bar{E}$

mean energy

$$\boxed{\bar{E}(t) \to \bar{E}^{eq}(S, \bar{V})}$$

You have reached equil. under the constraint of $\alpha_1, \ldots, \alpha_{L+1}$ fixed: potential $\Psi^{eq}(\alpha_1, \ldots, \alpha_{L+1})$



Slowly change one $\alpha_i(t)$ in time (keeping $\alpha_{j\neq i}$ fixed) such that we remain approx in equil. throughout

$(\dot{S}^i \approx 0)$

slowly $\Leftrightarrow$ "quasistatically"

while this occurs: $\dot{\bar{E}} - T(t)\dot{S} + \sum_{\nu} f_{\nu}(t)\dot{\bar{x}}_{\nu} = -T\dot{S}^i \approx 0$

$\Rightarrow$ implies some nonzero change $\dot{\Psi} \neq 0$

$\Rightarrow$ can calculate $\frac{\dot{\Psi}}{\dot{\alpha}_i} = \frac{\frac{d\Psi}{dt}}{\frac{d\alpha_i}{dt}} \approx \left.\frac{\partial \Psi^{eq}}{\partial \alpha_i}\right|_{\alpha_{j\neq i}}$

Pressure example:

i) $G^{eq}(T, P)$ let $T(t)$ change slowly
keep P fixed

$$\dot{\bar{E}} - T(t)\dot{S} + P\dot{\bar{V}} \approx 0$$

$$G(t) = \bar{E} - TS + P\bar{V}$$

$$\dot{G} + \dot{T}S \approx 0$$

$$\dot{G} \approx -\dot{T}S$$

$$\frac{\dot{G}}{\dot{T}} = \boxed{-S \approx \left.\frac{\partial G^{eq}}{\partial T}\right|_P}$$

ii) $G(T, P)$ let $P(t)$ change slowly
keep T fixed

$$\dot{\bar{E}} - T\dot{S} + P\dot{\bar{V}} \approx 0$$

$$\dot{G} - \dot{P}\bar{V} \approx 0$$

$$\Rightarrow \frac{\dot{G}}{\dot{P}} \approx \boxed{\bar{V} \approx \left.\frac{\partial G^{eq}}{\partial P}\right|_T}$$

By equality of 2nd deriv:

$$\frac{\partial^2 G^{eq}}{\partial T\,\partial P} = \boxed{\left.\frac{\partial \bar{V}}{\partial T}\right|_P = -\left.\frac{\partial S}{\partial P}\right|_T}$$

Maxwell relation

Similarly,

$$\frac{\partial^2 F^{eq}}{\partial T\,\partial \bar{V}} = \boxed{-\left.\frac{\partial S}{\partial \bar{V}}\right|_T = -\left.\frac{\partial P}{\partial T}\right|_{\bar{V}}}$$

$$\frac{\partial^2 H^{eq}}{\partial S\, \partial \underline{P}} = \boxed{\left.\frac{\partial T}{\partial \underline{P}}\right|_S = \left.\frac{\partial \bar{V}}{\partial S}\right|_{\underline{P}}}$$

Next question: if we change things arbitrarily quickly, are there any exact relationships known?

$\Rightarrow$ Jarzynski equality (1997)

Crooks fluctuation relation (1998)

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