Approaching equilibrium

Start w/ general principles that apply far from equil:

system at one temp. T

avg. work over traj.

2nd law: $$I = \Delta S - \frac{1}{T}\Delta E - \frac{1}{T}W \geq 0$$

avg. over traj. of length $t_I - t_0$

$$\Delta S = S(t_I) - S(t_0)$$

$$\vdots$$

$$S(t) = -k_B \sum_n p_n(t) \ln p_n(t)$$

$$E(t) = \sum_n p_n(t) E_n$$

look at traj. of one step: $\mu = (n_0, n_1)$

$t_0 = t \qquad t_I = t + \delta t$

divide by δt: $$\sigma = \frac{\Delta S}{\delta t} - \frac{1}{T}\frac{\Delta E}{\delta t} - \frac{1}{T}\frac{W}{\delta t} \geq 0$$

for small δt: $$\sigma = \dot{S} - \frac{1}{T}\dot{E} - \frac{1}{T}\dot{W} \geq 0 \qquad \text{Eq. (1)}$$

$$\dot{S} = \frac{dS}{dt} \qquad \dot{E} = \frac{dE}{dt}$$

equ. valid instataneously at any t

focus on conservative work: $$W(\mu) = \omega_{n_1 n_0} = f(x_{n_1} - x_{n_0})$$

$$\bar{W} = \langle \bar{W}(\mu) \rangle$$
$$\simeq f\big(x(t+\delta t) - x(t)\big)$$

"force" change in phys. quantity

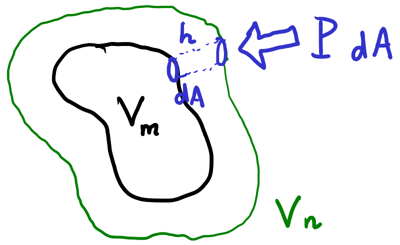
$$x(t) = \sum_n p_n(t)\, x_n \Rightarrow \dot{\bar{W}} = \frac{\bar{W}}{\delta t} \approx f\,\dot{x} = f\,\frac{dx}{dt}$$

more general: $\dot{\bar{W}} = \sum_{k=1}^{L} f_k \dot{x}_k$ L diff. forces

famous example: $x_n = V_n$ volume of sys. in state n

$x(t) = V(t)$ mean volume at time t

outside fluid/gas at press. P



work ω_{nm} in $m \to n$ trans:

$$\omega_{nm} = \int_{\substack{\text{surface} \\ \text{in state } m}} h\, P\, dA$$

$$= P \int h\, dA = P(V_n - V_m)$$

Eq. (1):
multiply by $-T$ & note it is valid at every instant, even if $T(t)$ & $f_k(t)$ vary w/ time:

Eq. $(*)$: $$\boxed{\underbrace{-T(t)\,\sigma}_{\leq 0} = \dot{E} - T\dot{S} + \sum_{k=1}^{L} f_k(t)\,\dot{x}_k}$$ true at all times

$=0$ iff equil.

Derive a zoo of thermodynamic potentials:

GOAL: make RHS of Eq. $(*)$ look like $\dot{\Psi}$

for some potential func. $\Psi(t)$

$2L+3$ terms: $\dot{E}$, $T(t)$, $\dot{S}$, $\{f_k(t), \dot{x}_k \quad k=1,\dots,L\}$

claim: if we constrain $L+1$ quantities (fix them at const. values)

$\Rightarrow$ either f_k or x_k is fixed for each work term

plus one of $E, T,$ or S

show: $\text{RHS} = \dot{\psi}$

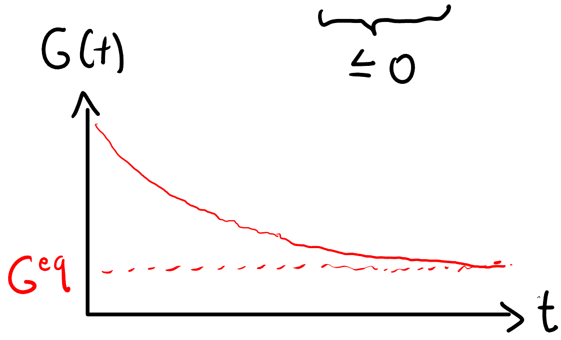
$+ \quad \psi(t) \xrightarrow[t\to\infty]{} \psi^{eq}\underbrace{(\alpha_1, \dots, \alpha_{L+1})}_{\text{fixed quantities}}$

concrete example: $L=1 \qquad \dot{W} = P(t)\dot{V}$

Eq. (*) $\Rightarrow \quad -T(t)\,\sigma = \dot{E} - T(t)\dot{S} + P(t)\dot{V}$

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

$$\underbrace{-T\sigma}_{\leq 0} = \dot{E} - T\dot{S} + P\dot{V} = \frac{d}{dt}\underbrace{(E - TS + PV)}_{\substack{G(t) \\ \text{Gibbs free energy}}}$$



$$\boxed{\begin{array}{c} G(t) \xrightarrow[t\to\infty]{} G^{eq}(T,P) \\ \text{decreases} \end{array}}$$

ii) fix T, V: $T(t) = T$, $\dot{V} = 0$

$$(*) \Rightarrow -T\sigma = \dot{E} - T\dot{S} = \frac{d}{dt}\underbrace{(E - TS)}_{\substack{F(t) \\ \text{Helmholtz free} \\ \text{energy}}}$$

$$\boxed{F(t) \xrightarrow[\substack{t\to\infty \\ \text{decr.}}]{} F^{eq}(T,V)}$$

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

$$-T\sigma = \dot{E} + P\dot{V} = \frac{d}{dt}\underbrace{(E + PV)}_{\substack{H(t) \\ \text{enthalpy}}}$$

$$\boxed{H(t) \xrightarrow[\substack{t\to\infty \\ \text{dec.}}]{} H^{eq}(S,P)}$$

note: $\dot{H} = \dot{E} + P\dot{V} = \dot{E} + \dot{W} = \dot{Q}$ total heat into sys.

if you want equil. w/ $\dot{H} = 0$

$\Rightarrow \dot{Q} = 0 \Rightarrow$ thermal isolation of sys, preventing heat flow

iv) fix S, V: $-T\sigma = \dot{E} = \frac{d}{dt}E(t)$

$\dot{S} = 0$, $\dot{V} = 0$

$$\boxed{E(t) \xrightarrow[\substack{t\to\infty \\ \text{decr.}}]{} E^{eq}(S,V)}$$