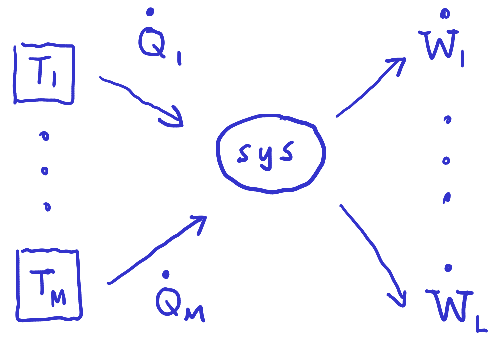
PHYS 414: 4-1-20



$$\dot{Q} = \dot{Q}_1 + \cdots + \dot{Q}_M$$

$$\dot{W} = \dot{W}_1 + \cdots + \dot{W}_L$$

$$\dot{Q} = \dot{\bar{E}} + \dot{W}$$

$$\dot{S} = \underbrace{\dot{S}^i}_{\geq 0} + \dot{S}^e = \dot{S}^i + \frac{\dot{Q}_1}{T_1} + \cdots + \frac{\dot{Q}_M}{T_M}$$

1) Often we look at stationary state: $p_n(t) \to p_n^s$

anything that depends directly on $p_n(t)$ & nothing else time-depend. will then become const.

$\dot{\bar{E}}, \dot{S} \to 0$

sys quantity A_n in state n

$$\bar{A} = \sum_n A_n p_n \to \dot{\bar{A}} = 0 \text{ in stat. state}$$

note: $\dot{\bar{A}} = \frac{1}{2} \sum_{nm} J_{nm} (A_n - A_m)$ using $\dot{p}_n = \sum_m J_{nm}$

$$= \frac{d}{dt} \bar{A} \to 0$$

2) stat. state $\begin{cases} \text{equil. stat. state} & \dot{S}^i = 0 \quad \text{ESS} \\ \text{non-equil. stat. state} & \dot{S}^i > 0 \quad \text{NESS} \end{cases}$

$$\dot{S}^i = \frac{k_B}{2} \sum_{nmk} J_{nm}^{(k)} \ln \frac{W_{nm}^{(k)} p_m}{W_{mn}^{(k)} p_n} = 0 \quad \text{in ESS}$$

$$\Leftrightarrow J_{nm}^{(k)} = 0 \quad \text{for all } (n,m)$$

$\boxed{\text{In ESS all dotted quantities are zero.}}$

Turn our attention to ESS ($\dot{S}^i = 0$) + also look near equilibrium ($\dot{S}^i \approx 0$).

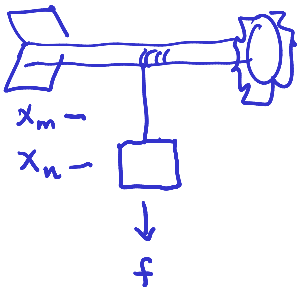
Narrow our focus to one heat bath (one temp. T) but still allow multiple work couplings.

Consider the case where work coupling

$$V^{(\nu)}_{nm} = f_\nu (x_{\nu n} - x_{\nu m})$$

$\nu = 1, \dots, L$ $\qquad$ $x_{\nu n}$ = ν th deg. of freedom in sys. state n

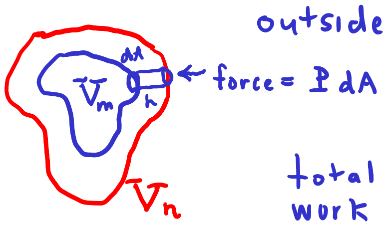
Examples: a)



work $= f(x_n - x_m)$

b) V_n is the volume of sys. in state n

outside fluid/gas pressure P (const.)



$$\underset{\text{in } m \to n \text{ trans.}}{\text{total work}} = \int_{\substack{\text{surf.}\\ \text{in state } m}} h \, P \, dA$$

$$= P(V_n - V_m)$$

Allow for generality the temp. $T(t)$

+ work coupling factors $f_\nu(t)$

to be time-dep. in general (i.e. $P(t)$)

$\Rightarrow$ all our formalism is valid instantaneously

MR: $$\frac{W_{nm}(t)}{W_{mn}(t)} = \exp\left[-\frac{1}{k_B T(t)}\Big(E_n - E_m + \overbrace{\sum_\nu f_\nu(t)\,(x_{\nu n} - x_{\nu m})}^{V_{nm}}\Big)\right]$$

$$\dot{S} = \dot{S}^i + \dot{S}^e = \dot{S}^i + \frac{\dot{Q}}{T(t)}$$

$$\dot{Q} = \dot{E} + \dot{W}$$

combine into one equ. to rule all of undergrad thermo.

note: $$\bar{x}_\nu = \sum_n p_n(t)\, x_\nu$$

$$\dot{\bar{x}}_\nu = \frac{1}{2}\sum_{nm} J_{nm}(t)\,(x_{\nu n} - x_{\nu m})$$

$$\dot{W} = \frac{1}{2}\sum_{nm\nu} J_{nm} V_{nm}^{(\nu)} = \sum_\nu f_\nu(t)\,\dot{\bar{x}}_\nu$$

"thermodynamic" force

analogous to power ~ force · velocity

$$-T(t)\dot{S}^i = \dot{Q} - T(t)\dot{S}$$

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

valid instant. at all times (not just in stat. state)

$\Rightarrow$ use this to derive the entire zoo of thermo. potentials

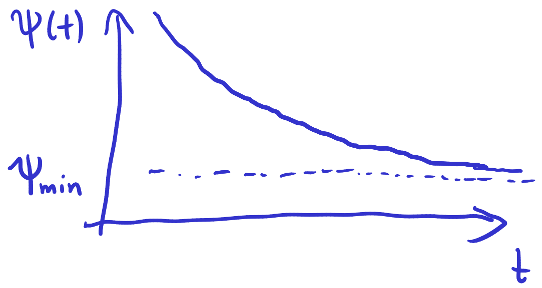
$\Rightarrow$ " " derive Maxwell relations

Next time: • make RHS of equ. look like $\dot{\Psi}$, the time der. of some potential func. Ψ

$$\Rightarrow -T(t)\dot{S}^i = \dot{\Psi} \leq 0 \quad \text{b/c} \quad T(t) > 0, \ \dot{S}^i \geq 0.$$

$\Psi(t)$ cannot increase, $\dot{\Psi} = 0$ can only occur in ESS ($\dot{S}^i = 0$)

If Ψ is bounded from below (min. possible value)



$t \to \infty$ $\quad \dot{S}^i \to 0$ $\quad \Rightarrow$ approach ESS

$\dot{\Psi} \to 0$

Explore properties of Ψ_{min}