$$\boxed{\bar{W}(\bar{A}) = W(A) - \bar{A}A} \qquad \bar{A} = \frac{\partial W(A)}{\partial A}$$

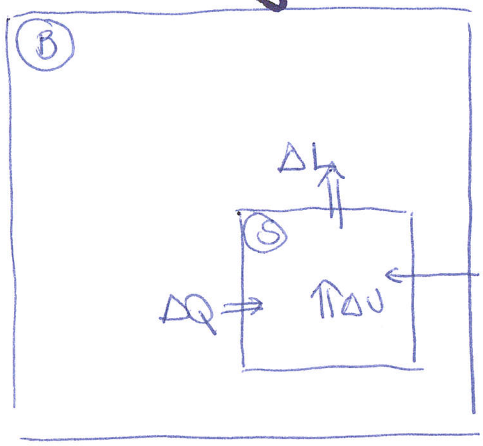
$$\frac{\partial \bar{W}}{\partial \bar{A}} = -A \qquad d\bar{W} = dW - \bar{A}\,dA - A\,d\bar{A}$$

but $dW = \bar{A}\,dA$

$$d\bar{W} = \bar{A}\,dA - \bar{A}\,dA - A\,d\bar{A}$$

1

Thermodynamics of a system in a bath



Bath $P_0\ T_0\ x_0$ intensive

System $P\ T\ x$

$V\ S\ X$ extensive

B+S is isolated

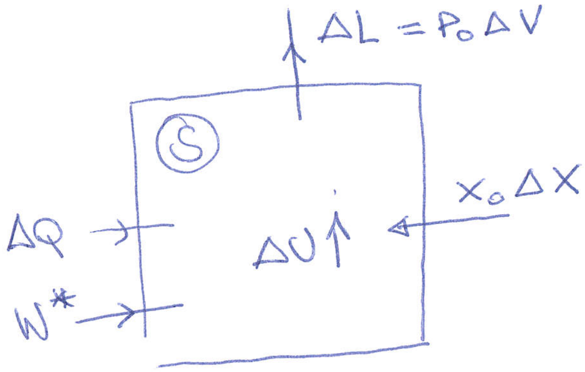
Stability: equilibrium is

$P_0 = P \quad T_0 = T_0 \quad x_0 = x$

will a small deviation from these value decay?

Fluctuations: if the system is stable what are the small fluctuations of P, T, x w.r.t. $P_0\ T_0\ x_0$?

Availability



$T_0 \Delta S \geq \Delta Q$

Source temperature

$$\Delta U = \Delta Q - \Delta L + x_0 \Delta X + W^*$$

$$W^* + \Delta Q = \Delta U + P_0 \Delta V - x_0 \Delta X$$

$$W^* + T_0 \Delta S \geq \Delta U + P_0 \Delta V - x_0 \Delta X$$

$$W^* \geq \Delta U + P_0 \Delta V - x_0 \Delta X - T_0 \Delta S$$

def: $A = U + P_0 V - T_0 S - x_0 X \qquad U = U(S, V, X)$

$$\Delta A = \Delta U + P_0 \Delta V - T_0 \Delta S - x_0 \Delta X \leq W^*$$

$$A(S, V, X; T_0\ P_0\ x_0)$$

$$-\Delta A \geq -W^*$$

$-\Delta A$ = maximum work we can extract from the system in a Bath $P_0 T_0 x_0$

proceed with $\cancel{x_0 = 0}$ $\Delta X = 0$ No input eg. $\cancel{\Delta N = 0}$

$\Rightarrow$ closed system

$$A = U + P_0 V - T_0 S - x_0 X \neq G = U + PV - TS \cancel{-\mu N}$$

$$dU = \underbrace{TdS - PdV}_{\text{System}}$$

Equilibrium

$$dA = TdS - PdV + P_0 dV - T_0 dS$$

$$= (T - T_0) dS - (P - P_0) dV$$

equilibrium

$$T = T_0 \quad P = P_0 \Rightarrow dA = 0$$

$$\left(\frac{\partial A}{\partial S}\right)_V = T - T_0 = 0 \qquad \left(\frac{\partial A}{\partial V}\right)_S = P_0 - P = 0$$

Stability $\Rightarrow$ convexity of A

$$o) \; H = \begin{pmatrix} \frac{\partial^2 A}{\partial S^2} & \frac{\partial^2 A}{\partial S \partial V} \\ \frac{\partial^2 A}{\partial V \partial S} & \frac{\partial^2 A}{\partial V^2} \end{pmatrix} \qquad \det H \geq 0 \text{ stability}$$

stability along "S" $\quad \frac{\partial^2 A}{\partial S^2} \geq 0 \qquad (a)$

stability along "V" $\quad \frac{\partial^2 A}{\partial V^2} \geq 0 \qquad (b)$

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a) Stability along "S"

$$\frac{\partial^2 A}{\partial S^2} = \left(\frac{\partial T}{\partial S}\right)_V = \frac{(\partial T/\partial U)_V}{(\partial S/\partial U)_V} = \frac{1/C_V}{1/T} = \frac{T}{C_V} \geq 0$$

$$C_V \geq 0$$

b) stability along "V"

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_S = -\left(\frac{\partial P}{\partial V}\right)_S \geq 0$$

def $\quad k_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$ ~~isother~~ isoentropic compressibility

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_S = \frac{1}{V k_S} \geq 0$$

$$k_S \geq 0$$

c)
$$\begin{vmatrix} \left(\frac{\partial T}{\partial S}\right)_V & \left(\frac{\partial T}{\partial V}\right)_S \\ -\left(\frac{\partial P}{\partial S}\right)_V & -\left(\frac{\partial P}{\partial V}\right)_S \end{vmatrix} \geq 0$$

is a jacobian $= \dfrac{\partial(T; -P)}{\partial(S; V)}$

Jacobian identity

$$\frac{\partial(A;B)}{\partial(C;D)} = \frac{\partial(A;B)}{\partial(X;D)}\frac{\partial(X;D)}{\partial(C;D)}$$

then

$$\frac{\partial(T;-P)}{\partial(S;V)} = \frac{\partial(T;-P)}{\partial(T;V)}\frac{\partial(T;V)}{\partial(S;V)}$$

$$\frac{\partial(T;-P)}{\partial(T;V)} = \begin{vmatrix} 1 & \cancel{\left(\frac{\partial T}{\partial V}\right)_T} \\ -\left(\frac{\partial P}{\partial T}\right)_V & -\left(\frac{\partial P}{\partial V}\right)_T \end{vmatrix} = -\left(\frac{\partial P}{\partial V}\right)_T$$

$$\frac{\partial(T;V)}{\partial(S;V)} = \begin{vmatrix} \left(\frac{\partial T}{\partial S}\right)_V & \left(\frac{\partial T}{\partial V}\right)_S \\ \cancel{\left(\frac{\partial V}{\partial S}\right)_V} & \underbrace{\left(\frac{\partial V}{\partial V}\right)_S}_{1} \end{vmatrix} = \left(\frac{\partial T}{\partial S}\right)_V$$

$$\frac{\partial(T;-P)}{\partial(S;V)} = -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial T}{\partial S}\right)_V \geq 0$$

but $\left(\frac{\partial T}{\partial S}\right)_V = \frac{(\partial T/\partial U)_V}{(\partial S/\partial U)_V} = \frac{T}{C_V}$ from a) ≥ 0

def $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ isothermal compressibility

$$-\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{V\kappa_T} \Rightarrow \boxed{\kappa_T \geq 0}$$

a) stability along "S"

"force" (intensive) $T \longleftrightarrow S$ Response (extensive) $(V = \text{const})$

$C_V \geq 0 \quad \Rightarrow \quad \left(\frac{\partial^2 U}{\partial S^2}\right)_V \geq 0$ U convex in S

b) stability along "V"

$P \longleftrightarrow V \quad (S = \text{const})$

$\kappa_S \geq 0 \quad \Rightarrow \quad \left(\frac{\partial^2 H}{\partial P^2}\right)_S \leq$ H concave in S

c) stability overall

$P \longleftrightarrow V \quad (T = \text{const})$

$\kappa_T \geq 0 \quad \Rightarrow \quad \left(\frac{\partial^2 G}{\partial P^2}\right)_T \leq 0$ G concave along P