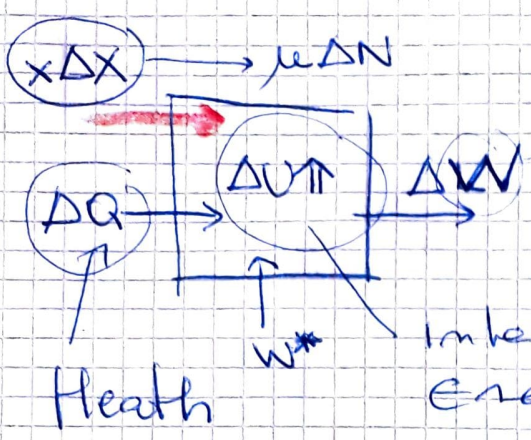


Work

1st principle

Conservation of Energy

Heath is energy

$$\Delta Q = \Delta L + \Delta U$$

Some extra work EXERTED to the System

$$\Delta Q + x\Delta X + W^* = \Delta U + \Delta W$$

exchange of matter

Internal energy

Work done

2nd principle

not all Heat can be converted in Work

$$\eta = \frac{W \rightarrow \text{produced work}}{Q \leftarrow \text{absorbed heat}}$$

$\eta < 1 \Leftarrow$ Carnot cycle (the best)

$$\Delta S \geq \int_A^B \frac{dQ}{T}$$

$= \text{reversible}$ $\quad \Delta S \geq 0$, Isolated

Thermodynamic Potential

for a certain set of ext condition

$\Delta W \leq 0$ ← 1st

W thermodyn potential

= reversible ← 2nd

Isolated

$\Delta S \geq 0$ $\quad W = -S$

under which conditions ?

→ Conserved energy
→ Conserved # of particles
→ fixed volume

E
N
V
} Natural Variables

$S(E, V, N)$ thermodynamic potential

Change ext condition → change potential

→ fixed temperature
→ conserved # of particle
→ fixed volume

T
N
V
} Nat vars

$$F(T, V, N) = U - TS$$

$$\Delta F = \Delta U - \Delta(TS)$$

fixed T $\quad \Delta(TS) = T\Delta S$

fixed V $\quad \Delta U = \Delta Q - \Delta W$

$$\Delta W = P\Delta V = 0$$

$$\Delta U = \Delta Q$$

} 1st prnc

thus

$$\Delta F = \Delta Q - T\Delta S \leq 0$$

} 2nd prnc

$$dF(T,V,N) = -SdT - PdV + \mu dN \quad (+ x dX)$$

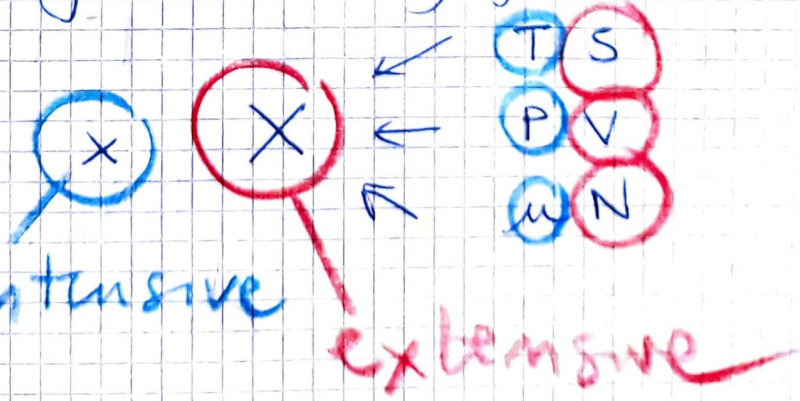
$$\left(\frac{\partial F}{\partial T}\right)_{VN} = -S$$

Infinitessmal change

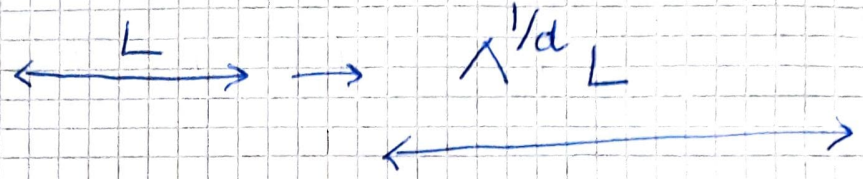
$$dF = dU - d(TS) = dQ - pdV - TdS - SdT$$

(forgetting about external sources)

Thermodynamic Conjugation



Size (scale) transformation



such that

$V \rightarrow \lambda V$

$N \rightarrow \lambda N$

extensive $\rightarrow \lambda$ extensive

while

intensive $\rightarrow$ intensive

Relations btw Thermodynamic Potentials

↳ Legendre Transform

change ext conditions

$T\,V\,N \rightarrow F$

$T\,P\,N \rightarrow G = F + PV$

pair of thermodynamic conjugate variables

$$dG = dF + d(PV)$$

$$dG = \cancel{dQ} - \cancel{pdV} - TdS - \cancel{SdT} + \cancel{pdV} + VdP$$

$$dG = -SdT + VdP + \mu dN$$

generally speaking

if W is a thermodynamic potential in the variable A

i.e. $W(A)$ such that $\bar{A} = \frac{\partial W}{\partial A}$

we want to change $A \to \bar{A}$

and therefore $W \to \bar{W}$

$$\bar{W}(\bar{A}) = W(A) - \bar{A}A$$

such that

$$A = -\frac{\partial \bar{W}}{\partial \bar{A}}$$

Legendre Transform

indeed

$$d\bar{W} = dW - \bar{A}dA - AdA = \cancel{\bar{A}dA} - \cancel{\bar{A}dA} - AdA$$

In classical mechanics

$$\underbrace{H(pq)}_{\text{Hamiltonian}} = p\dot{q} - \underbrace{\mathcal{L}(q\dot{q})}_{\text{Lagrangian}}$$

Maxwell's Identities

W is a thermodynamic potentials in 2 variables

$$W(A, B)$$

W is a state function i.e. dW is an exact differential

↳ $$\frac{\partial^2 W}{\partial A \partial B} = \frac{\partial^2 W}{\partial B \partial A}$$

if A is thermo-conjug to $\bar{A}$

B is thermo conjug to $\bar{B}$

then

$$\frac{\partial W}{\partial A} = \bar{A} \qquad \frac{\partial W}{\partial B} = \bar{B}$$

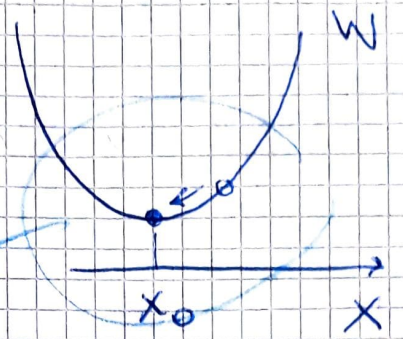
$$\left(\frac{\partial \bar{A}}{\partial B}\right)_A = \left(\frac{\partial \bar{B}}{\partial A}\right)_B$$

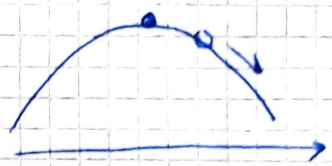
example let $W = F$ $A = T$ $B = V$

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V} \Rightarrow -\left(\frac{\partial S}{\partial V}\right)_{TN} = -\left(\frac{\partial P}{\partial T}\right)_{VN}$$

Thermodynamic Stability | (7)

stability



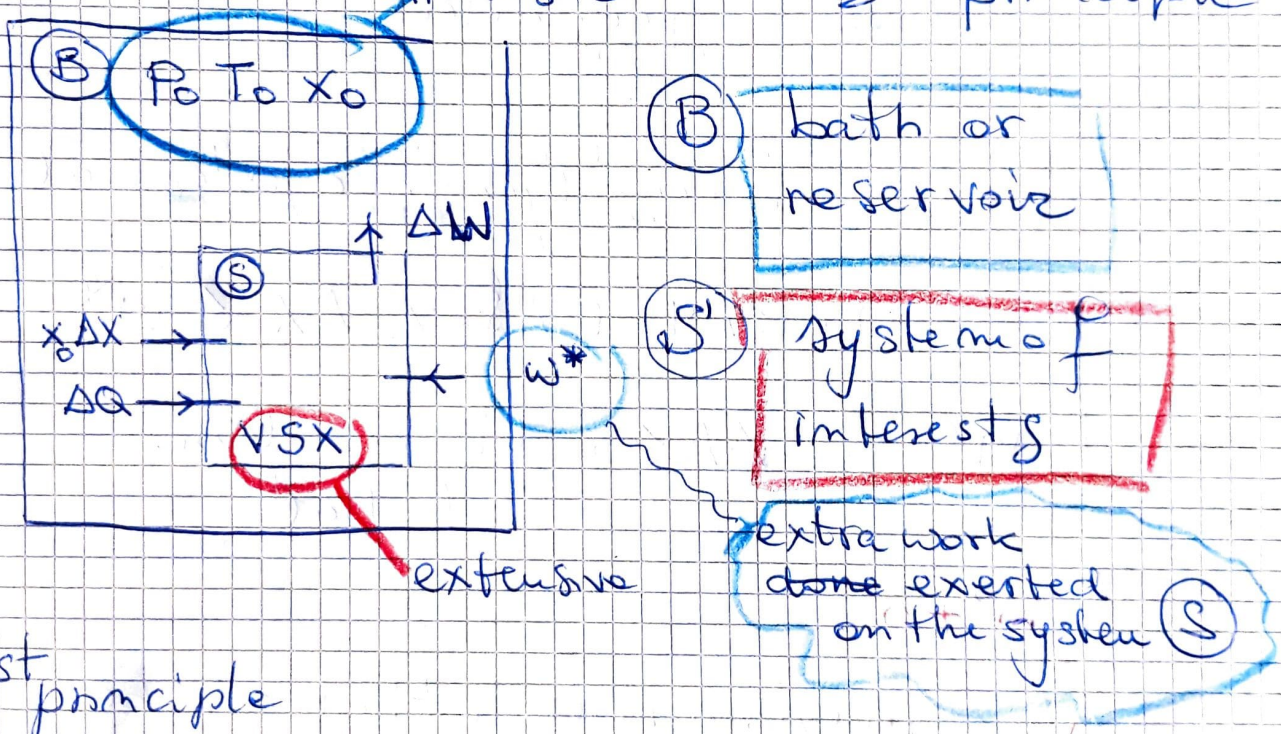


stable

unstable

Mechanical Analogy

→ Dissipation 2nd principle



1st principle

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

delta's small fluctuations

2nd principle

$$T_0 \Delta S \geq \Delta Q$$

small fluctuations as transformation at constant reservoir temperature

$$\Delta W = P_0 \Delta V$$

~~XXXX~~

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

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

Availability

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

$$A(\underbrace{S, V, X}_{\text{variables}}; \underbrace{T_0 P_0 x_0}_{\text{parameters}})$$

System — Reservoir

a mixed thermodynamic potential

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

if $W^* = 0$ $\Delta A \leq 0$ thermodyn. potential

if $W^* \neq 0$

$-\Delta A$ = maximum work that can be extracted by a system at $P_0 T_0 x_0$

proceed with $\Delta X = 0$ e.g. a closed system $(x_0 = \mu_0 \; X = N)$

$$A = U + P_0 V - T_0 S$$

$$dA = dU + P_0 dV - T_0 dS$$

$$dA = \overbrace{TdS - PdV} + P_0 dV - T_0 dS$$

$$\boxed{dA = (T - T_0)dS - (P - P_0)dV} \quad \left(+ (X - X_0) dX\right)$$

equilibrium

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

at equilibrium

$$\left(\frac{\partial A}{\partial S}\right)_V = \left(\frac{\partial A}{\partial V}\right)_S = 0 \Rightarrow \begin{cases} T = T_0 \\ P = P_0 \\ (X = X_0) \end{cases}$$

stability:

Convexity of A

Hessian determinant $\begin{Vmatrix} \frac{\partial^2 A}{\partial S^2} & \frac{\partial^2 A}{\partial S \partial V} \\ \frac{\partial^2 A}{\partial V \partial S} & \frac{\partial^2 A}{\partial V^2} \end{Vmatrix} \geq 0$

stability along "S" $\longrightarrow \frac{\partial^2 A}{\partial S^2} \geq 0$

stability along "V" $\longrightarrow \frac{\partial^2 A}{\partial V^2} \geq 0$

a) Stability along "S"

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

$$\boxed{C_V \geq 0}$$

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

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

$$\boxed{\kappa_S \geq 0}$$

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

Jacobian identity

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

then

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

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

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

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

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

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

a) stability along "S"

"force" (intensive) T ⟷ S' Response (extensive) (V = const)

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

b) stability along "V"

P ⟷ V (S = const)

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

c) stability overall

P ⟷ V (T = const)

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

Thermodynamic Responses & Stability

$$d(\text{Response}) = \left(\frac{d\,\text{Response}}{d\,\text{ext Force}}\right) d\,\text{ext Force}$$

System Response

ext "force" intensive

Thermodynamic Response

Thermodynamic Stability → definite sign of thermodyn. Response

a) stability along "S"

$$(dS)_V = \left(\frac{\partial S}{\partial T}\right)_V dT$$

$$\left(\frac{dT}{dS}\right)_V = \frac{T}{C_V} = \left(\frac{\partial^2 U}{\partial S^2}\right) \geq 0 \qquad U \text{ convex (along } S)$$

b) stability along "V"

$$(dV)_S = \left(\frac{\partial V}{\partial P}\right)_S dP$$

$$\left(\frac{\partial V}{\partial P}\right)_S = -V\kappa_S = \left(\frac{\partial^2 H}{\partial P^2}\right)_S \leq 0 \qquad H \text{ concave (along } P)$$

c) overall stability

$$(dV)_T = \left(\frac{\partial V}{\partial P}\right)_T dP \qquad \left(\frac{\partial V}{\partial P}\right)_T = -V\kappa_T = \left(\frac{\partial^2 G}{\partial P^2}\right)_T \leq \qquad G \text{ concave (along } P)$$