

Second Law: Heat Flows Spontaneously from High Temperatures to Low Temperatures

①

equivalent statements:

- * Spontaneous tendency of a system to go toward thermodynamic equilibrium cannot be reversed without at the same time changing some organised energy, work, into disorganised energy heat
- * in a cyclic process it is not possible to convert heat from a hot reservoir into work without at the same time transferring some heat to a colder reservoir
- * the entropy change of any system and its surroundings, considered together, is positive and approaches zero for any process which approaches reversibility

importance:

- 1.) can calculate the maximum efficiency of an engine which converts heat into work
- 2.) enables the introduction of a new state variable

S - entropy

entropy - provides means for determining stability of equilibrium states

- gives measure of the degree of disorder in a system

- link between reversible and irreversible processes

Carnot engine

(2)

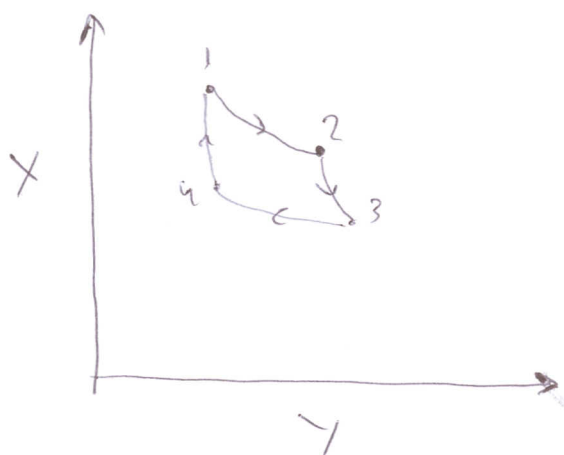
- heat engines: based on observation that if heat is allowed to flow from a hot reservoir to a cold reservoir part of it can be converted into work

Carnot: temperature differences can also disappear spontaneously without producing work

⇓
Carnot engine is based on reversible processes, i.e. wasteful heat flows are eliminated

Steps of Carnot engine

- isothermal absorption of heat ΔQ_{12} from a hot (τ_h) reservoir ($1 \rightarrow 2$)
- adiabatic expansion and cooling $\tau_h \rightarrow \tau_c$ ($2 \rightarrow 3$)
- isothermal expulsion of heat ΔQ_{43} into ~~a reservoir~~ cold reservoir (τ_c)
- adiabatic return to initial state τ_h ($4 \rightarrow 1$)



work done - area contained between lines $1 \rightarrow 2$ $2 \rightarrow 3$ $3 \rightarrow 4$ $4 \rightarrow 1$
(integral under curves)

total efficiency: $\eta = \frac{\Delta W_{\text{tot}}}{\Delta Q_{12}}$ work done divided by heat absorbed (3)

U , internal energy, is a state variable, so $\Delta U = 0$

$$\Delta U = \Delta Q_{\text{tot}} - \Delta W_{\text{tot}} = 0$$

$\Downarrow$

$$\Delta W_{\text{tot}} = \Delta Q_{12} + \Delta Q_{34} = \Delta Q_{12} - \Delta Q_{43}$$

$$\text{efficiency: } \eta = 1 - \frac{\Delta Q_{43}}{\Delta Q_{12}}$$

no engine can have an efficiency of $\eta = 1$, in which all heat is converted into work, as shown below

proof that Carnot engine is the most efficient engine operating

- consider two heat engines A and B between two reservoirs ~~that add~~
- both A and B run between same reservoirs

T_h and T_c

- assume that A is an engine with irreversible processes
- assume that B is a Carnot engine
- suppose we line the two engines so that they perform the same amount of work

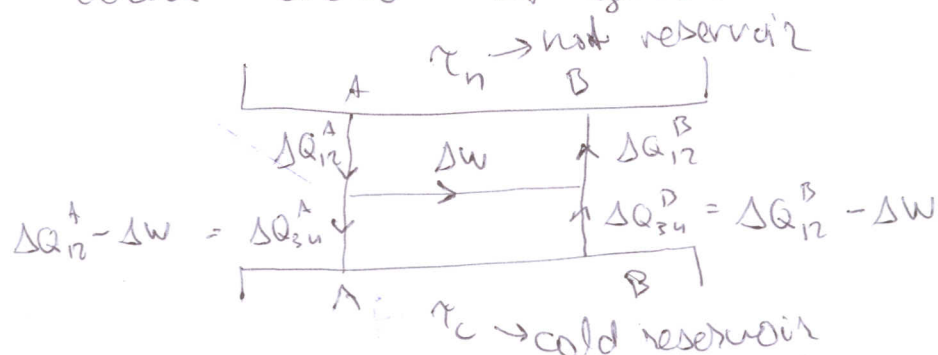
$$\Delta W_A = \Delta W_B$$

assume for now that $\eta_A > \eta_B \rightarrow$ engine A is more efficient than engine B

$$\Downarrow$$

$$\frac{\Delta W}{\Delta Q_{12}^A} > \frac{\Delta W}{\Delta Q_{12}^B} \Rightarrow \Delta Q_{12}^B > \Delta Q_{12}^A$$

- One can run the Carnot engine as a refrigerator
 - since Carnot engine is reversible, efficiency is the same
- couple Carnot refrigerator to engine A so that the work generated by engine A is used to drive Carnot refrigerator



- heat transferred to cold reservoir

$$(\Delta Q_{12}^A - \Delta W) - (\Delta Q_{12}^B - \Delta W) = \Delta Q_{12}^A - \Delta Q_{12}^B$$

$$\text{if } \eta_A > \eta_B \Rightarrow \Delta Q_{12}^B > \Delta Q_{12}^A \Rightarrow \Delta Q_{12}^A - \Delta Q_{12}^B < 0$$

$\Rightarrow$ heat transferred to cold reservoir would be negative $\rightarrow$ contradicts the second law

$\Downarrow$

$\Downarrow$

No engine running between two reservoirs can be more efficient than the Carnot engine, and all Carnot engines have the same efficiency

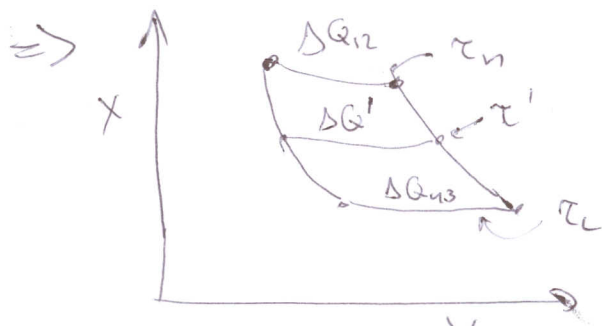
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Next step: we can introduce a temperature scale

- we can write $\frac{\Delta Q_{43}}{\Delta Q_{12}} = f(\tau_n, \tau_c)$

- we could also operate two Carnot engines

One between τ_n and τ' the other between τ' and τ_c



$$\frac{\Delta Q'}{\Delta Q_{12}} = f(\tau_n, \tau')$$

$$\Rightarrow f(\tau_n, \tau_c) = f(\tau_n, \tau') + f(\tau', \tau_c)$$

$$\frac{\Delta Q_{43}}{\Delta Q'} = f(\tau', \tau_c)$$

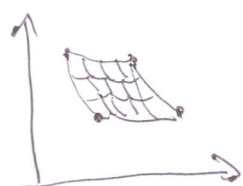
$$\Rightarrow \frac{\Delta Q_{43}}{\Delta Q_{12}} = f(\tau_n, \tau_c) = g(\tau_n) g^{-1}(\tau_c)$$

$\Rightarrow g(\tau)$ is some function of temperature

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = \frac{\tau_c}{\tau_n} \quad g(\tau) = \frac{1}{\tau} \quad (\text{Kelvin scale})$$

$$\Rightarrow \frac{\Delta Q_{43}}{\tau_c} - \frac{\Delta Q_{12}}{\tau_n} = 0 \Rightarrow \frac{\Delta Q_{12}}{\tau_n} + \frac{\Delta Q_{34}}{\tau_c} = 0$$

BUT! we can consider many infinitesimal Carnot cycles coupled together



$$\Rightarrow \oint \frac{dQ}{T} = 0$$

(cyclic process consisting of reversible processes)

entropy: $dS = \frac{dQ}{T}$

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state variable since it is an exact differential

- if an engine contains irreversible processes

$$\Rightarrow \frac{\Delta Q_{43}}{\Delta Q_{12}} > \frac{T_c}{T_h} \quad \left(\eta = 1 - \frac{\Delta Q_{43}}{\Delta Q_{12}} < 1 - \frac{T_c}{T_h} \right)$$

$\Downarrow$

$$\frac{\Delta Q_{12}}{T_h} + \frac{\Delta Q_{43}}{T_c} < 0 \Rightarrow \oint \frac{dQ}{T} < 0$$

- evaluating entropy change:

if process is reversible $\Rightarrow$

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

if process is irreversible $\rightarrow$ one can not use the formula along the path since only the inequality

$$\oint \frac{dQ}{T} < 0 \text{ is valid}$$

solution: construct reversible path between endpoints (hypothetical)

$$\text{and use } \Delta S = \int_A^B \frac{dQ}{T}$$

- an irreversible process does not contain all entropy contributions, since

$$\int_{\text{irrev}} \frac{dQ}{T} < \int_{\text{rev}} \frac{dQ}{T}$$

~~irreversibility~~

$$dS = \frac{dQ}{T} + d_i S$$

$d_i S$ - entropy due to spontaneous processes

for a reversible process: $d_i S = 0$

for an isolated system: $dQ = 0 \Rightarrow dS = d_i S \geq 0$

equality holds for reversible processes (spontaneous)

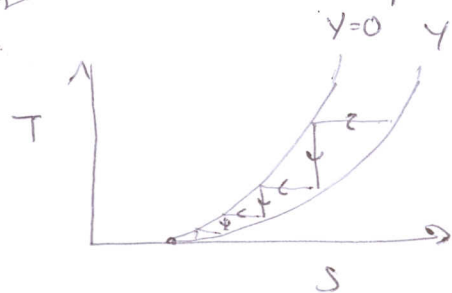
equilibrium state: state which is stable against spontaneous changes $\Rightarrow dS=0$ or maximum entropy state
(maximum entropy principle)

Third Law of Thermodynamics: the difference in Entropy Between States Connected by a Reversible Process Goes to Zero in the Limit $T \rightarrow 0K$

- roughly speaking $\rightarrow$ system at zero temperature falls into its ground state $\Rightarrow$ entropy goes to zero (or its lowest value)

$\Rightarrow$ consequence: it is impossible to reach zero in a finite number of steps using reversible processes

consider $T-S$ curves for different values of some generalized force Y



we know that

$$\left(\frac{\partial T}{\partial Y}\right)_{S,N} = - \left(\frac{\partial T}{\partial S}\right)_{Y,N} \left(\frac{\partial S}{\partial Y}\right)_{T,N}$$

$$\text{stability condition } \left(\frac{\partial S}{\partial T}\right)_{Y,N} \geq 0$$

- as curves approach each other an infinite number of steps will be needed

- other consequence of third law - certain derivatives of S become zero: example $dS = \left(\frac{\partial S}{\partial Y}\right)_{T,N} dY$ at $T=0$

Fundamental Equation of Thermodynamics

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- entropy: measure of disorder
- entropy can be obtained from state counting for an isolated system $\Rightarrow$ proportional to the number of microstates
pure state $\rightarrow$ zero entropy

- entropy: extensive / additive quantity

first-order homogeneous function of the extensive variables of the system

$$S(\lambda U, \lambda X, \{\lambda N_i\}) = \lambda S(U, X, \{N_i\})$$

increase all extensive variables $\Rightarrow$ entropy will increase (proportionally)

second law: $\frac{dQ}{T} \leq dS$

$$dQ \leq T dS$$

first law: $dU = dQ - dW$

$$dU + dW \leq T dS$$

$$dU - Y dX - \sum_i \mu_i' dN_i \leq T dS$$

- consider the reversible case

$$\frac{d}{d\lambda} (\lambda S) = \frac{\partial S}{\partial (\lambda U)} \frac{d}{d\lambda} (\lambda U) + \frac{\partial S}{\partial (\lambda X)} \frac{d}{d\lambda} (\lambda X) + \sum_i \frac{\partial S}{\partial (\lambda N_i)} \frac{d}{d\lambda} (\lambda N_i)$$

$\Downarrow$

$\Downarrow$

$$\frac{\partial S}{\partial U} = \frac{1}{T}$$

$$\frac{\partial S}{\partial X} = -\frac{Y}{T}$$

$$\frac{\partial S}{\partial N_i} = -\frac{\mu_i}{T}$$

} equations of state

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$$\Rightarrow TS = U - YX - \sum_j \mu_j' N_j \quad (\text{definition of internal energy})$$

take differential

$$T dS + S dT$$

$$= dU - X dY - Y dX - \sum_j d\mu_j' N_j - \sum_j \mu_j' dN_j$$

 $\Downarrow$ $\Downarrow$

$$S dT + 0 = -X dY - \sum_j N_j d\mu_j'$$

Gibbs-Duhem equation

relates differentials of intensive variables

Thermodynamic Potentials

in mechanics: work can be stored as potential energy

in thermodynamics: work can be stored as thermodynamic potential, but for different sets of constraints thermodynamic potentials are different

other name for thermodynamic potentials $\Rightarrow$ free energies

Internal energies

$$U = TS + YX + \sum_j \mu_j' N_j$$

total differential form

$$dU = T dS + Y dX + \sum_j \mu_j' dN_j$$

for reversible changes

$$T = \left(\frac{\partial U}{\partial S} \right)_{X, \{N_j\}}$$

$$Y = \left(\frac{\partial U}{\partial X} \right)_{S, \{N_j\}}$$

$$\mu_j' = \left(\frac{\partial U}{\partial N_j} \right)_{S, \{N_{j \neq j}\}}$$

- can also derive relation between response functions (10)

$$\left[\frac{\partial}{\partial x} \left(\frac{\partial U}{\partial S} \right)_{x, \{N_j\}} \right]_{S, \{N_j\}} = \left[\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial x} \right)_{S, \{N_j\}} \right]_{x, \{N_j\}}$$

$\Downarrow$

$\Downarrow$

$$\left(\frac{\partial T}{\partial x} \right)_{S, \{N_j\}} = \left(\frac{\partial \mu_j}{\partial S} \right)_{x, \{N_j\}}$$

similarly

$$\left(\frac{\partial T}{\partial N_j} \right)_{S, x, \{N_{i \neq j}\}} = \left(\frac{\partial \mu_j}{\partial S} \right)_{x, \{N_j\}}$$

$$\left(\frac{\partial \mu_j}{\partial N_j} \right)_{S, x, \{N_{i \neq j}\}} = \left(\frac{\partial \mu_j}{\partial x} \right)_{S, \{N_j\}}$$

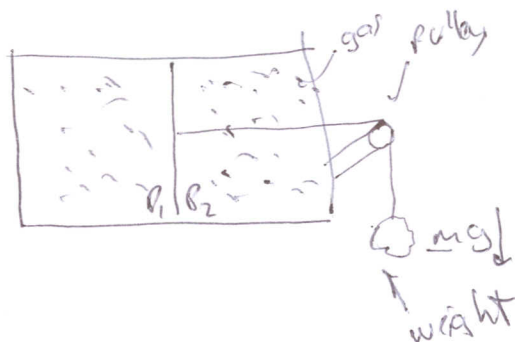
and

$$\left(\frac{\partial \mu_j}{\partial N_i} \right)_{S, x, \{N_{i \neq i}\}} = \left(\frac{\partial \mu_i}{\partial N_j} \right)_{S, x, \{N_{i \neq j}\}}$$

maxwell relations

- internal energy: for processes carried out reversibly in an isolated, closed system at fixed x and $\{N_j\}$ the change in internal energy is equal to the maximum amount of work that can be done on or by the system

example PVT system:



$$\Delta U = \Delta Q - \Delta W$$

for reversible process

$$\Delta Q = T \Delta S$$

- gas can do work on weight
- box is insulated / divided into two parts
- to do work reversibly - add infinitesimal increments to mass m

- no chemical reaction $\Delta U_i = 0$
- no change in size of the box $\Delta V = 0$
- reversible process $\rightarrow S T dS = \Delta Q$

isolated system $\rightarrow \Delta Q = 0$

$\Downarrow$

$$\Delta U = -\Delta W$$

work can be stored in the form of internal energy and can be recovered completely

irreversible process @ constant $S, V, \{U_i\} \rightarrow$ have to allow leakage of heat through walls

$$S dU = \Delta U = \Delta Q - \Delta W < S T dS - \Delta W$$

$\Downarrow$

$$\Delta U < -\Delta W$$

irreversible process: increase weight by a finite amount and allow it to drop suddenly

$\Downarrow$

in general $\Delta U \leq -\Delta W$

if no work is done $\Rightarrow \Delta U \leq 0$

internal energy either remains fixed or decreases

@ equilibrium system cannot change its state spontaneously

$\Rightarrow$ equilibrium state at fixed $S, V, \{U_i\}$ is a state of minimum internal energy

other thermodynamic potentials are obtained by
a Legendre transformation of U

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examples:

1. enthalpy: $H = U - XY = ST + \sum_j \mu_j' N_j$

$$(\Delta H)_{S, Y, \{N_j\}} \leq -\Delta W$$

at fixed $S, Y, \{N_j\} \rightarrow$ ~~stable~~ equilibrium state is
that of minimum enthalpy

2. Helmholtz free energy

$$A = U - TS = XY + \sum_j \mu_j' N_j$$

$$(\Delta A)_{T, X, \{N_j\}} \leq -\Delta W$$

equilibrium state at fixed $T, X, \{N_j\}$
 $\Rightarrow$ state of minimum A

3. Gibbs free energy

$$G = U - TS - XY = \sum_j \mu_j' N_j$$

$$(\Delta G)_{T, Y, \{N_j\}} \leq -\Delta W$$

equilibrium state at fixed $T, Y, \{N_j\}$
is a state of minimum ~~ΔG~~ G

4. Grand potential

$$\Omega = U - TS - \sum_j \mu_j' N_j = -XY$$

$$(\Delta \Omega)_{T, X, \{\mu_j'\}} \leq -\Delta W$$

equilibrium state at fixed $T, X, \{\mu_j'\}$
is a state of minimum Ω

Response functions

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- specific heats at constant volume / pressure

$$C_V = \left(\frac{dQ}{dT} \right)_V \quad C_P = \left(\frac{dQ}{dT} \right)_P$$
$$= T \left(\frac{dS}{dT} \right)_V \quad C_P = T \left(\frac{dS}{dT} \right)_P$$

- isothermal and adiabatic compressibilities

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad K_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S$$

- coefficient of thermal expansion

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

- to derive relations between response functions

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

$$\stackrel{||}{T \left(\frac{\partial S}{\partial T} \right)_P} = T \left(\frac{\partial S}{\partial T} \right)_V + \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

$$C_P = C_V + T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

Maxwell relations $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$

identity: $\left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial V}{\partial P} \right)_T = -1$

$$C_P - C_V = T \left[\frac{-1}{\left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial P}{\partial T} \right)_T} \right] \left(\frac{\partial V}{\partial T} \right)_P = -T \left[\left(\frac{\partial P}{\partial V} \right)_T \right] \left[\left(\frac{\partial V}{\partial T} \right)_P \right]^2$$

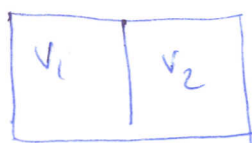
$$= + \frac{TV \alpha^2}{K_T}$$

similarly $\rightarrow K_T - K_S = -\frac{1}{V} \left(\frac{\partial V}{\partial S} \right)_P \left(\frac{\partial S}{\partial P} \right)_T \frac{TV \alpha^2}{C_P}$

$$\Rightarrow \frac{C_P}{C_V} = \frac{K_T}{K_S}$$

Equilibrium and Stability Conditions

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two systems in contact with each other
intuitively expect that pressure, temperature, etc.
tend to equalize at equilibrium

- obtain from maximum entropy principle

$$S = S_1(E_1, V_1) + S_2(E_2, V_2)$$

$$dS = \frac{\partial S_1}{\partial E_1} dE_1 + \frac{\partial S_1}{\partial V_1} dV_1 + \frac{\partial S_2}{\partial E_2} dE_2 + \frac{\partial S_2}{\partial V_2} dV_2$$

but ~~since~~ since $dE = 0 = dE_1 + dE_2$ $dV = 0 = dV_1 + dV_2$

$$dS = \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) dE_1 + \left(\frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} \right) dV_2$$

maximum entropy principle: $dS = 0$

$$\frac{\partial S_1}{\partial E_1} = \frac{1}{T_1} \Rightarrow \frac{1}{T_1} = \frac{1}{T_2} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

- one can also show that all generalized forces of two systems in equilibrium must be equal

- requiring the entropy to be a maximum leads to stability conditions

$$G_1(P_0, T_0) = E_1 - T_0 S_1 + P_0 V_1$$

- second order expansion

$$\delta G_1 = \delta S_1 \left(\frac{\partial E_1}{\partial S_1} - T_0 \right)$$

$$+ \delta V_1 \left(\frac{\partial E_1}{\partial V_1} + P_0 \right)$$

$$+ \frac{1}{2} \left[(\delta S_1)^2 \frac{\partial^2 E_1}{\partial S_1^2} + 2(\delta S_1)(\delta V_1) \left(\frac{\partial^2 E_1}{\partial S_1 \partial V_1} \right) + (\delta V_1)^2 \frac{\partial^2 E_1}{\partial V_1^2} \right] > 0$$

$\Rightarrow$

(Gibbs free energy)
of a system in contact
with a large reservoir
which holds P_0, T_0 fixed

at equilibrium

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$$\delta G_1 = \frac{1}{2} \left[(\delta S_1)^2 \frac{\partial^2 E_1}{\partial S_1^2} + 2(\delta S_1)(\delta V_1) \frac{\partial^2 E_1}{\partial S_1 \partial V_1} + (\delta V_1)^2 \frac{\partial^2 E_1}{\partial V_1^2} \right] > 0$$

$$\begin{array}{ccc} \text{true if} & \frac{\partial^2 E}{\partial S^2} > 0 & \frac{\partial^2 E}{\partial V^2} > 0 & \frac{\partial^2 E}{\partial S^2} \frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S \partial V} \right)^2 > 0 \\ & \downarrow & \downarrow & \downarrow \\ & \left(\frac{\partial T}{\partial S} \right)_V > 0 & - \left(\frac{\partial P}{\partial V} \right)_S = \frac{1}{\chi} > 0 & \frac{T}{V \chi_S \chi_V} > \left(\frac{\partial T}{\partial V} \right)_S^2 \\ & \downarrow & & \\ & \frac{T}{C_V} > 0 & \frac{1}{V \chi_S} > 0 & \end{array}$$

- similar stability criteria can be obtained from the other thermodynamic potentials
- stronger condition than requiring the entropy to be at maximum is to require that the entropy be a concave function of any of its generalized displacements
 - $\Downarrow$ global stability criteria