

# Postulate of Maximum Entropy

①

- in the way thermodynamics was presented in lecture 1B  $\Rightarrow$  existence of entropy function is postulated (distinct from 1A, there, the analysis of the Carnot cycle gives rise to a new state variable  $\rightarrow$  call it entropy)
- but here we postulate it, ~~study~~ its existence and mathematical properties, and show that they lead to the same results as the derivation in 1A (~~same as~~ usual statement of the second law, usual results for Carnot cycle)
- to define entropy correctly, first we define the concept of internal constraint
- consider isolated system divided into two subsystems

$N_1, V_1$	$N_2, V_2$
$E_1$	$E_2$

in this case  $N = N_1 + N_2$

$$E = E_1 + E_2$$

$$V = V_1 + V_2$$

(all three variables are extensive)

- the piston which divides system into two sub-systems creates the following constraints ②

\* fixed: prevents flow of energy between subsystems in the form of work

\* adiabatic: prevents the flow of ~~work~~ energy between subsystems in the form of heat

\* impermeable: prevents the flow of particles between subsystems

- we can ~~render~~ render the piston mobile, diathermic, or permeable  $\Rightarrow$  we can relax any number of the above constraints

- experiment: - start with piston which is fixed, adiabatic, impermeable / allow equilibration  
- relax one or more constraints / allow equilibration

- what can we say about this equilibration process, in particular about the new and old equilibrium states?



# Principle of Maximum Entropy

③

- postulates about properties of the entropy function

\*  $S(E, V, N)$  - positive and differentiable increasing function of  $E$  for fixed  $V, N$

\* for a system made of  $M$  subsystems

$$S_{\text{tot}}(E, V, N) = \sum_{m=1}^M S(E_m, V_m, N_m)$$

Note! the functional form is the same on both sides

\* Suppose the global isolated system is initially divided by internal constraints into subsystems separately in equilibrium. If one ~~or more~~ or more constraints are lifted the final entropy after equilibration must be greater than the initial entropy.

ENTROPY OF AN ISOLATED SYSTEM CAN NOT DECREASE!

- entropy defined for a system at equilibrium (far from equilibrium, no unique definition)

quasi-static process - process which takes place ④

infinitesimally close to equilibrium (during the entire process)

- infinitely slow, (idealization)

- in practice one can proceed from state A to state B, w.t. small perturbations are made, and after each such small change, equilibrium is re-established

↓  
as a result entropy is a function of time  $S_{\text{tot}}(t)$   
(of the whole isolated system)

- consequence of the properties of the entropy function  $\Rightarrow$  entropy is a concave function of its arguments

- concave function  $f''(x) \leq 0$

or  $f\left(\frac{x_1+x_2}{2}\right) \geq \frac{f(x_1)+f(x_2)}{2}$

Proof by contradiction!

assume entropy is a strictly convex function

$\Rightarrow f''(x) > 0 \Rightarrow S''(E) > 0$

⇓

$$2S(E) < S(E+\Delta E) + S(E-\Delta E)$$

this last equation implies that we can



increase the entropy by introducing an internal constraint  $\Rightarrow$  contradicts definition of entropy (actually  $\Rightarrow$  this can occur at phase transition points) ⑤

Intensive variables: temperature, pressure, chemical potential

temperature  $T$ :  $\left. \frac{\partial S}{\partial E} \right|_{V, N} = \frac{1}{T}$

pressure  $P$ :  $\left. \frac{\partial S}{\partial V} \right|_{E, N} = \frac{P}{T}$

chemical potential  $\mu$ :  $\left. \frac{\partial S}{\partial N} \right|_{E, V} = -\frac{\mu}{T}$

derive these definitions from corresponding equilibria

### 1.) thermal equilibrium

experiment: - start with global isolated system divided into two subsystems

$$S_1(E_1, V_1, N_1), S_2(E_2, V_2, N_2)$$

- relax adiabaticity constraint

new equilibrium state must be an entropy

maximum  $dS = dS_1 + dS_2 = 0$

$$dS = \left. \frac{\partial S}{\partial E_1} \right|_{V_1, N_1} dE_1 + \left. \frac{\partial S}{\partial E_2} \right|_{V_2, N_2} dE_2 = 0$$

$$dE_1 = -dE_2$$

$$dS = \left[ \left. \frac{\partial S}{\partial E_1} \right|_{N, V_1} - \left. \frac{\partial S}{\partial E_2} \right|_{N, V_2} \right] dE_1 = 0$$

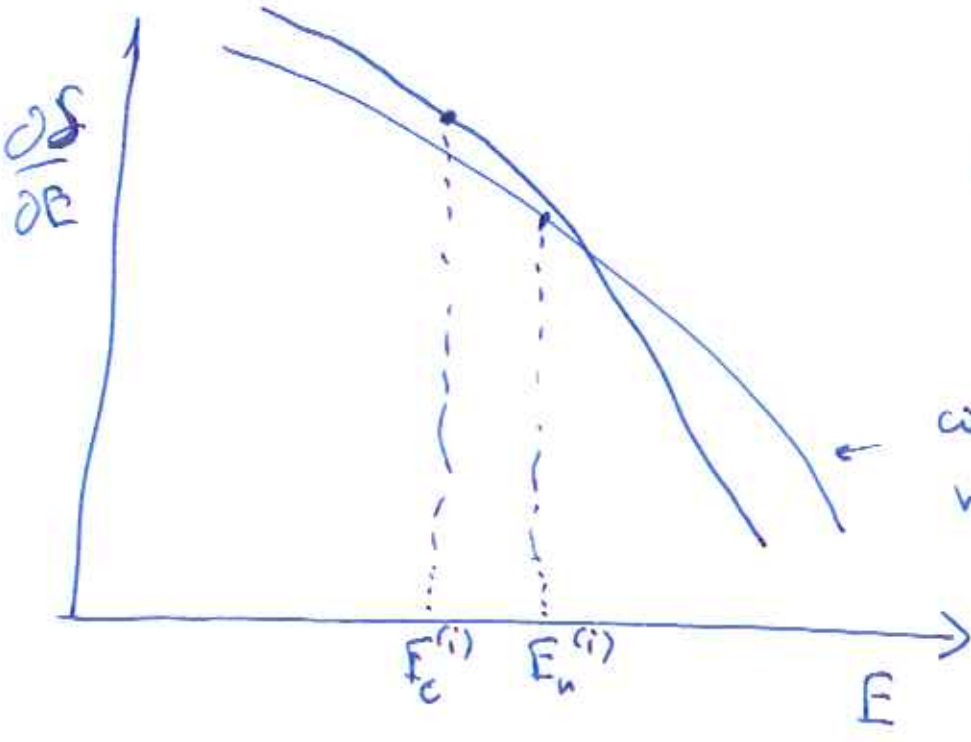
$$dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 = 0 \Rightarrow \boxed{T_1 = T_2} \Rightarrow \text{equilibrium}$$

- we can now show that energy flows from hot to cold (one way of stating the 2<sup>nd</sup> law of thermodynamics)

- consider two subsystems. hot  $T_h$  cold  $T_c$

- initially:  $T_c^{(i)} < T_h^{(i)} \Rightarrow \frac{1}{T_c^{(i)}} > \frac{1}{T_h^{(i)}}$

$$\Downarrow \\ E_c^{(i)} < E_h^{(i)}$$



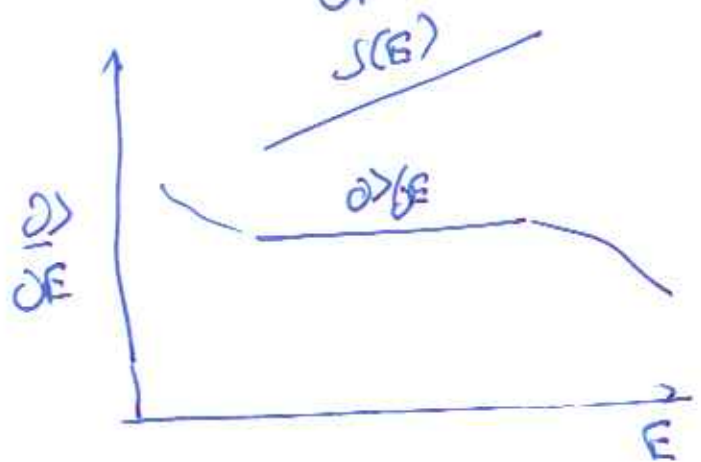
concave function, has to decrease since it is  $1/T$ , and temperature is an increasing function of  $E$

→ in this case system can only equilibrate (reach equal temperature) if heat flows from hot to cold (i.e.  $E_c^{(f)} > E_c^{(i)}$  and  $E_h^{(f)} < E_h^{(i)}$ )



case when  $\frac{\partial^2 S}{\partial E^2} = 0 \Rightarrow$  phase transition

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$$\Rightarrow \frac{\partial S}{\partial E} = \frac{1}{T}$$

$$\frac{\Delta S}{\Delta E} = \frac{1}{T} \Rightarrow \Delta E = T \Delta S$$

constant  
heat

- when a system is driven across a phase transition system's entropy is not changing as energy is being added  $\Rightarrow$  system is not homogeneous
- $\rightarrow$  as system is driven across phase transition, on one side phase 1, on the other side phase 2, it has to get from pure 1 to pure 2  $\Rightarrow$  inhomogeneous

~~Phase~~

## 2.) Thermal equilibrium

- same experiment but relax adiabaticity and fixed constraints

$$dS = \left( \frac{\partial S}{\partial E} \right)_{N_1, V_1} dE_1 + \left( \frac{\partial S}{\partial E} \right)_{N_2, V_2} dE_2 + \left( \frac{\partial S}{\partial V} \right)_{E_1, N_1} dV_1 + \left( \frac{\partial S}{\partial V} \right)_{E_2, N_2} dV_2$$

$$dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 + \left( \frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1 = 0$$

$\Rightarrow \boxed{T_1 = T_2} \quad \boxed{P_1 = P_2}$  at equilibrium

②

- we did not proceed "symmetrically"

- in the second we relaxed both adiabatic / fixed constraint, not just fixed

- if only fixed constraint is relaxed, there is still energy exchange in the form of work, since when one of the volumes increases at the expense of the other, they do work on each other

- if only fixed constraint is released  $\Rightarrow$  in the absence of friction between piston and container, piston will oscillate indefinitely

- if friction is considered  $\Rightarrow$  equilibrium state will have  $T_1 \neq T_2$

- consider  $T_1 = T_2 = T$  but  $P_2$  slightly larger than  $P_1$

$$dS = \left( \frac{P_1}{T_1} - \frac{P_2}{T_1} \right) dV_1 = \frac{(P_1 - P_2)}{T} dV_1 \stackrel{> 0}{\approx} 0$$

↑  
spontaneous  
process  
(equilibration)

if  $P_2 > P_1 \Rightarrow dV_1 < 0$

volume of subsystem with larger pressure

increases  $\Rightarrow$  expected (Note:  $T$  changes in this case but only as  $(dV_1)^2$ )



### 3.) particle flux equilibrium

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relax adiabaticity/impermeability constraints

$$dS = \left. \frac{\partial S}{\partial E_1} \right|_{V_1, N_1} dE_1 + \left. \frac{\partial S}{\partial E_2} \right|_{V_2, N_2} dE_2 + \left. \frac{\partial S}{\partial N_1} \right|_{E_1, V_1} dN_1 + \left. \frac{\partial S}{\partial N_2} \right|_{E_2, V_2} dN_2 = 0$$

$$dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 + \left( -\frac{\mu_1}{T_1} + \frac{\mu_2}{T_2} \right) dN_1 = 0$$

$$\boxed{T_1 = T_2} \quad \boxed{\mu_1 = \mu_2} \quad \text{at equilibrium}$$

Equation of state

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_V = \sigma_T(E, V) \quad \frac{P}{T} = \left. \frac{\partial S}{\partial V} \right|_E = \sigma_P(E, V)$$

$\sigma_T$  - strictly decreasing function of  $E$

$$\Rightarrow E = h(T, V)$$

$\Downarrow$

$$\boxed{\frac{P}{T} = \sigma_P(E(T, V), V) = g(T, V)} \Rightarrow \text{equation of state}$$

example:  $\frac{P}{T} = \frac{nR}{V}$  (ideal gas)

## Quasi-static and reversible processes

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$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\boxed{TdS = dE + PdV - \mu dN}$$

S - increasing function of E

$$\boxed{dE = TdS - PdV + \mu dN}$$

if  $dV = dN = 0$  (no work, no particle flux)

$$dE = TdS \Rightarrow \boxed{TdS = dQ}$$

- entropy = defined for equilibrium  $\Rightarrow$  all these equations are only valid for quasi-static processes

- there are other variables only defined for equilibrium (quasi-static process)

- consider work done during expansion of a gas

$$dW = F dx = \underbrace{P}_{P_{\text{ext}}} A dx = P_{\text{ext}} dV = - \underbrace{P}_{\substack{\uparrow \\ \text{pressure of gas}}} dV$$

if process is not quasi-static  $\Rightarrow$  pressure of gas is not a well-defined variable

$$dW = F dx = P_{\text{ext}} A dx = P_{\text{ext}} dV \Rightarrow \text{valid in general}$$



- 1<sup>st</sup> law: conservation of energy:  $dE = dQ + dW$  (11)  
always valid

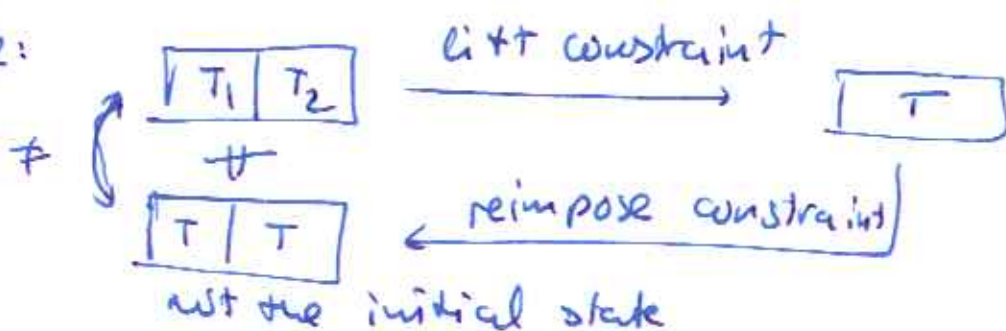
$dE = TdS + dW \Rightarrow$  only valid at equilibrium or  
 for a quasi-static process

reversible transformation: quasi-static transformation which takes place at fixed entropy

- in general: lifting one or more constraints  
 lifts entropy  $\Rightarrow S_{\text{final}} > S_{\text{initial}}$

$\rightarrow$  reimposing constraints can not return system to original state  $\Rightarrow$  irreversible

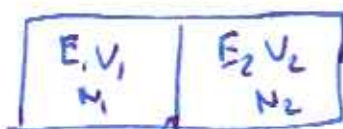
example:



- for isolated system process proceeds in one direction spontaneously

- for reversible transformation  $\Rightarrow$  can return to initial state, by modification of constraints

example:



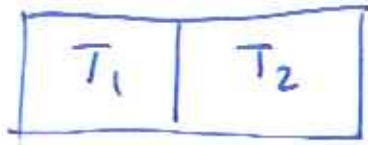
infinitesimal motion of ~~barrier~~  
 barrier

- quasi-static process without heat exchange  
 $\Rightarrow$  reversible:  $dQ = 0 = TdS \Rightarrow dS = 0$  ✓

example of quasi-static transformation

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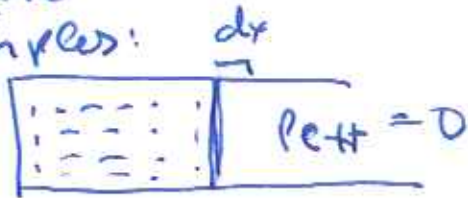
which is not reversible:



wall is almost adiabatic  
(heat flow is very slow)  
entropy  $S \rightarrow$  increases

infinitesimal transformation is not necessarily quasi-

static  
examples:



entropy change:  $dS = \frac{pRdx}{V}$   
adiabatic but not reversible  
 $dS \geq 0$



very small hole

$\Rightarrow$  at the end  
entropy  $\sim R \ln 2$