13th KIAS-APCTP Winter School on Statistical Physics

Rigorous Thermodynamics and the Entropy Principle

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Main references

[LY1] Lieb & Yngvason, Phys. Rep. **310**, 1 (1999)

[T] Thess, *The Entropy Principle* (Springer, Berlin, 2011)

Another references

[B] Boyling, Proc. R. Soc. Lond. A **329**, 35 (1972)

[C] H. B. Callen, *Thermodynamics and an Introduction to Thermostatics* (John Wiley & Sons, Singapore, 1985)

[LY2] Lieb & Yngvason, Phys. Today **53**, 32 (2000)

[LY3] Lieb & Yngvason, Proc. R. Soc. A **469**, 20130408

[note] Supplements for the lecture note.

If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations — then so much the worse for Maxwell's equations. If it is found to be contradicted by observation — well these experimentalists do bungle things sometimes. But if your theory is found to be against **the second law of thermodynamics** I can give you no hope; there is nothing for it but to collapse in deepest humiliation.

–Sir Arthur Stanley Eddington

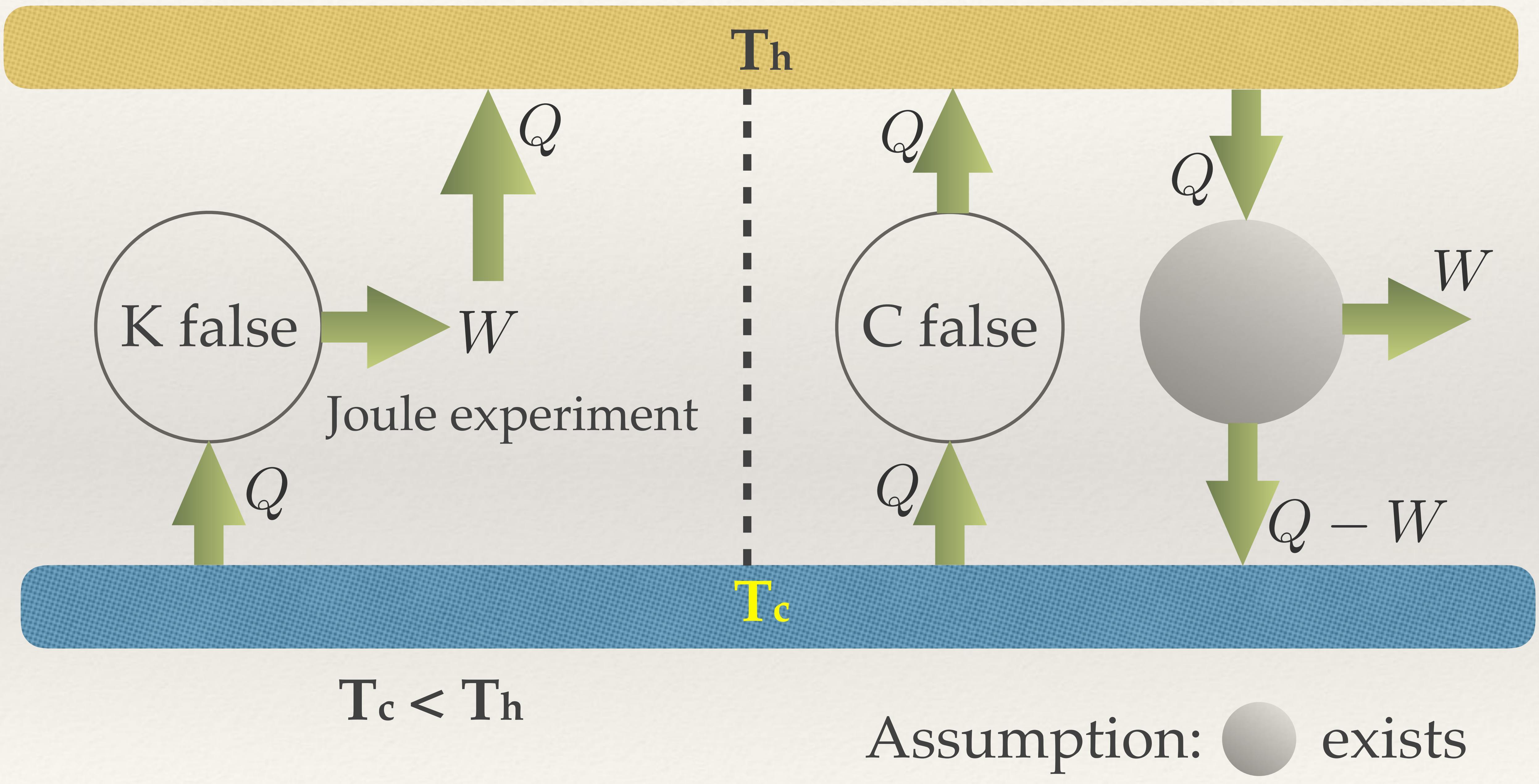
Why do we (I?) care about rigor?

- *Ideal theory* has played an important role in physics.
- If the law of entropy increase is ever going to be derived from statistical mechanics — a goal that has so far eluded the deepest thinkers — then it is important to be absolutely clear about ***what it is that one wants to derive***. ([LY1] page 5) **"Guiding principle"**
- Recall a recent controversy about Gibbs vs Boltzmann entropy definitions. [J. Dunkel and S. Hilbert, Nat. Phys. **10**, 67 (2013)]

“The” 2nd law of thermodynamics

- *Clausius* : No process is possible, the *sole result* of which is that **heat** is transferred from a body to a **hotter** one.
- *Kelvin* (*and Planck*) : No process is possible, the *sole result* of which is that a body is **cooled** and work is done.
- *Carathéodory* : In any **neighborhood** of any state there are states that cannot be reached from it by an **adiabatic** process.

Equivalence of C and K [Huang]



How to teach statistical thermal physics in an introductory physics course

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AJP **69**, 68 (2001)

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In an age when a single atom can be trapped and manipulated the teaching of thermal physics starting from the empirical laws of thermodynamics is a pedagogical scandal. It is now high time to reform the style of teaching thermal physics in introductory college physics courses.

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

late the two expressions. The Clausius definition of entropy is one of the most difficult subjects to teach. First of all, T in the above expression (1) is the absolute temperature. If it were not the absolute temperature in expression (1) the Clausius definition would be meaningless. However, the concept of absolute temperature is never fully explained in textbooks that follow the traditional style of instruction. The temperature is usually introduced through an operational definition which cannot explain the significance of the absolute temperature other than as a curious experimental fact. We cannot convey the significance of absolute temperature without a basic understanding of its statistical nature.

How to define physical quantity

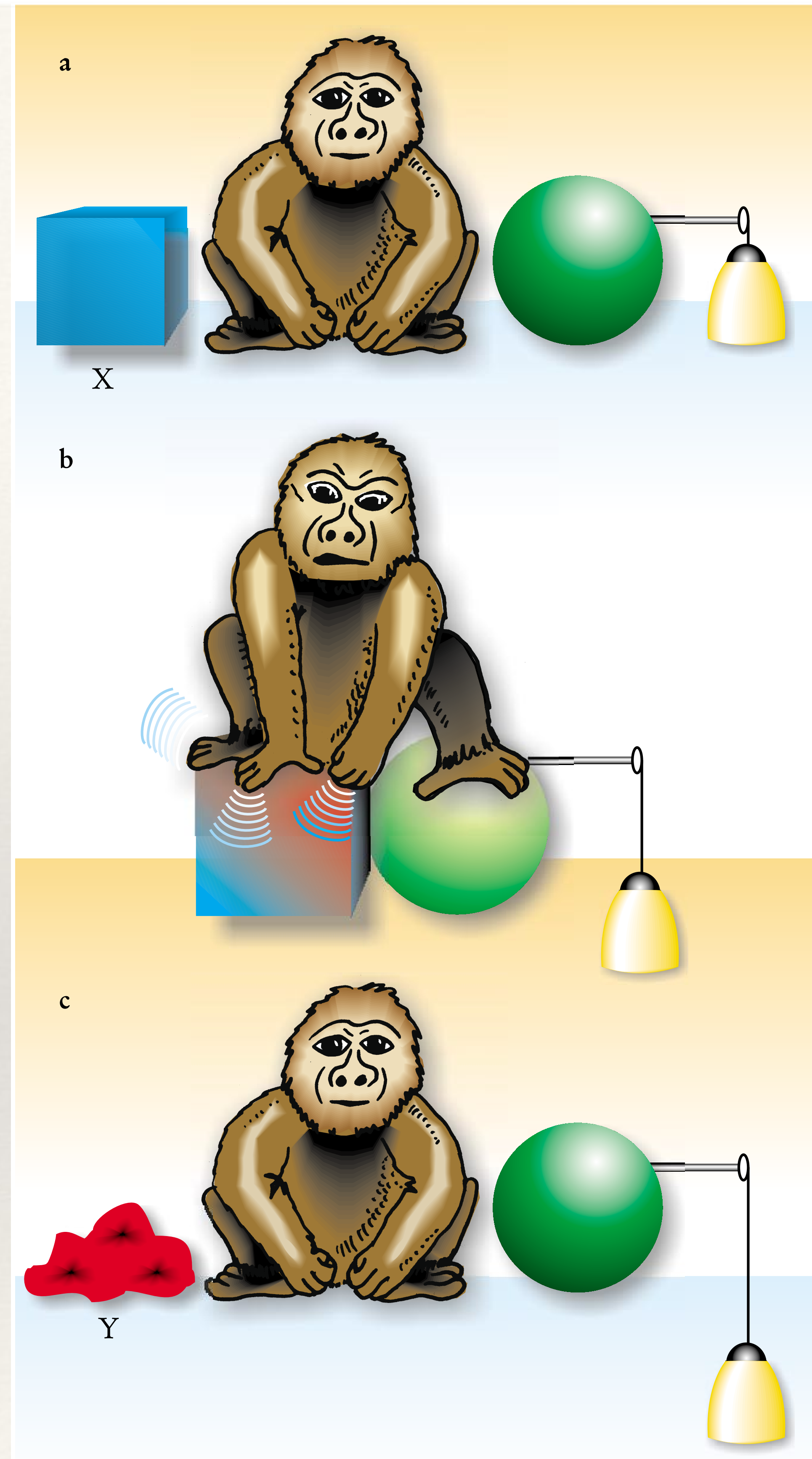
- First, we need an order relation.
- Second, we need an addition of two systems.
- Example: To define inertial mass
  - Step 1: Inelastic collision (to define order)

  - Step 2: addition (to define quantity)

$n \vdash m \vdash n+1$

Entropy Principle

Basic Concepts
Adiabatic accessibility
General Axioms
Constructing Entropy



Basic Concepts: Primitive Terms

Equilibrium

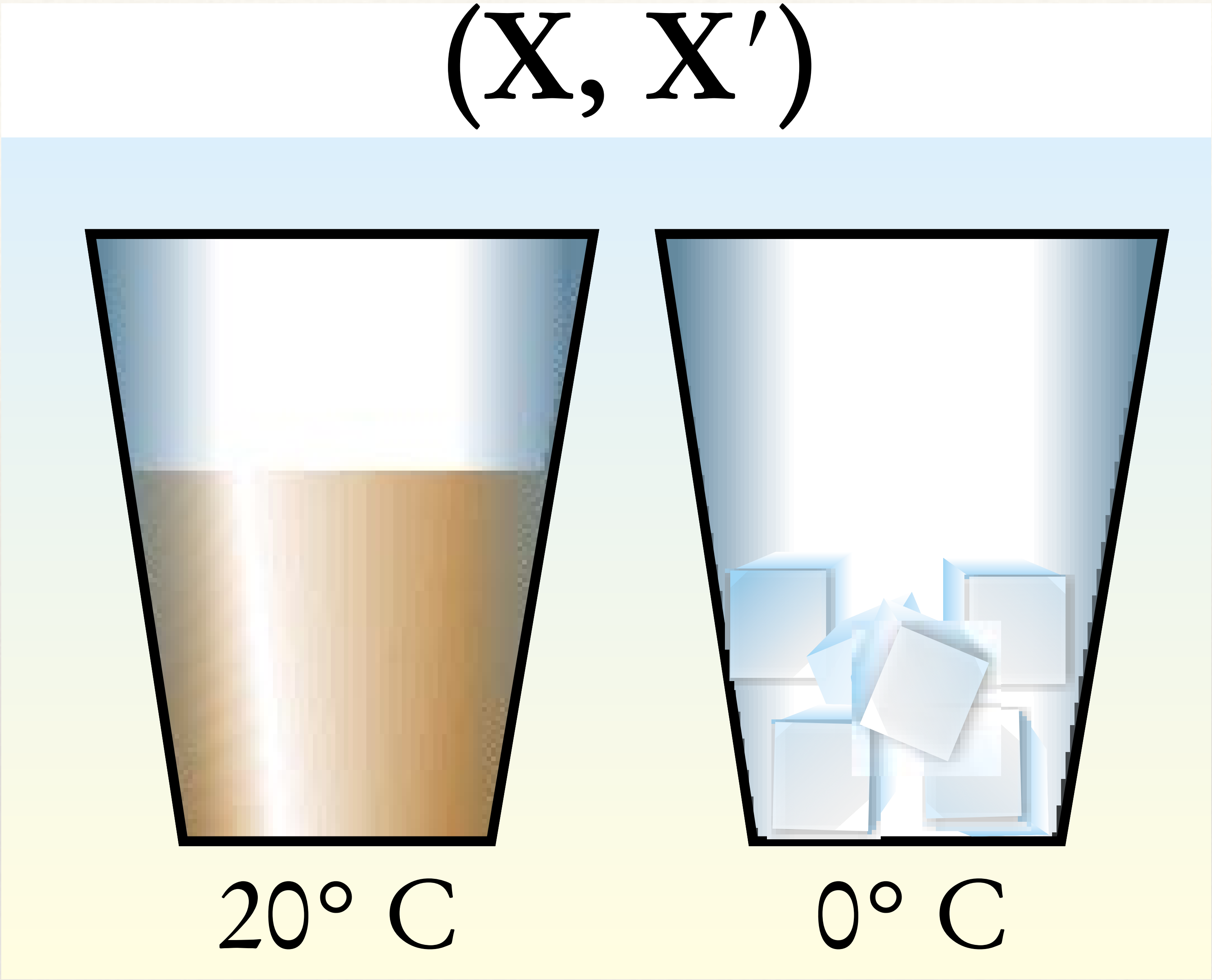
- We are mainly interested in equilibrium systems.
- But what is an equilibrium state?
    - Homogeneous? not necessarily.
    - Steady state with temperature gradient? (à la Fourier)
    - In practice the criterion for equilibrium is circular; *Operationally, a system is in an equilibrium state if its properties are consistently described by thermodynamic theory.* [C]

States and systems

- Macroscopic, neither microscopic nor astronomical, system. By state X is meant a macroscopic state.
- Equilibrium states are our main concern.
- System Γ : a collection of all possible (equilibrium) states
- Compound system : Cartesian Product of systems

$$\Gamma_1 \times \Gamma_2 = \Gamma_2 \times \Gamma_1, \quad (X_1, X_2) \in \Gamma_1 \times \Gamma_2$$

- Subsystems may or may not interact with each other



Example of a compound system (From [LY2])

Scaling

- Scaled copy (scaled space)

$$\Gamma^{(t)} = t\Gamma : \text{If } X \in \Gamma, tX \in \Gamma^{(t)}$$

- Physically, tX is a state with scaled energy, volume, chemical substances, and so on. $\Gamma^{(t)}$ is a space with *scaled chemical substances*.

$$s(tX) = stX, \quad \left(\Gamma^{(t)}\right)^{(s)} = \Gamma^{(ts)}, \;\; \Gamma^{(1)} = \Gamma, \quad 1X = X$$

$$(\Gamma_1 \times \Gamma_2)^{(t)} = \Gamma_1^{(t)} \times \Gamma_2^{(t)} \qquad t(X_1, X_2) = (tX_1, tX_2)$$

Scaled product

- Scaled product

$$\Gamma_1^{(t_1)} \times \cdots \times \Gamma_N^{(t_N)} \text{ with points } (t_1 X_1, \ldots, t_N X_N)$$

- Multiple scaled copy of Γ

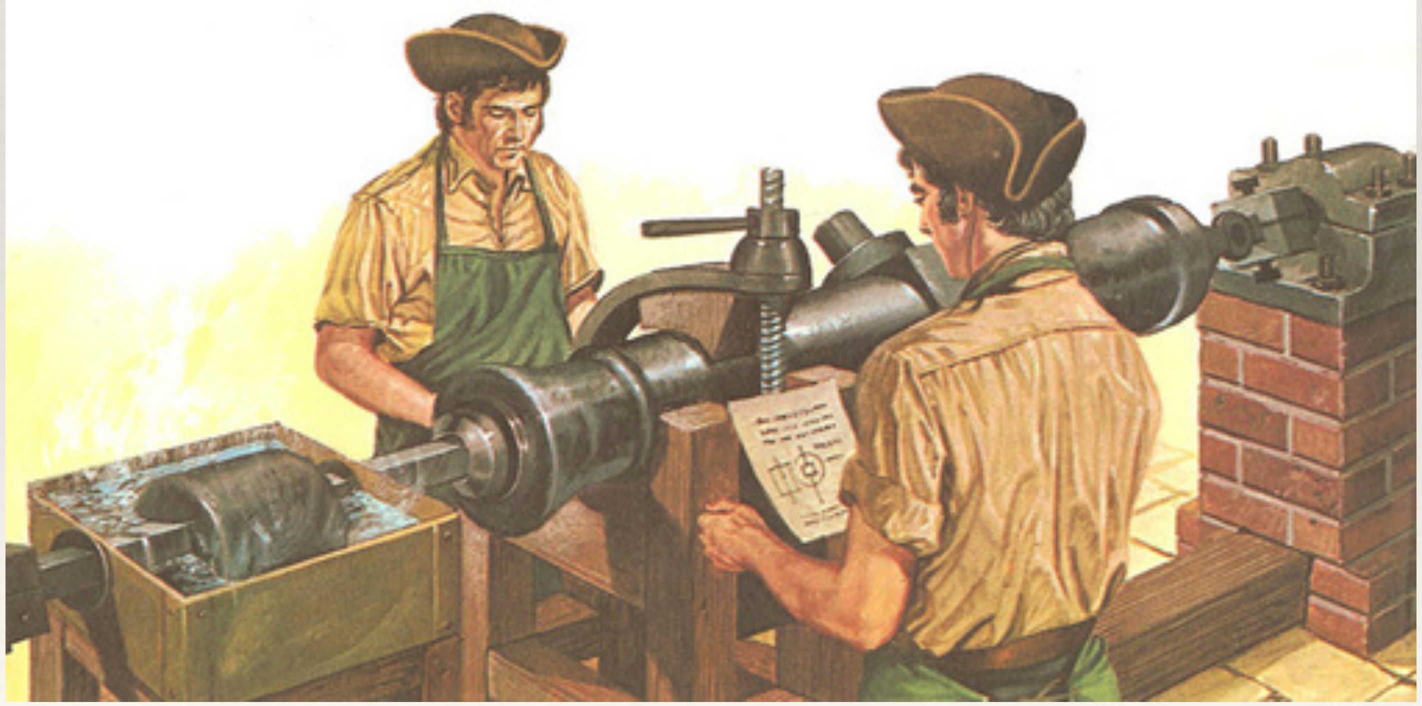
$$\Gamma^{(t_1)} \times \cdots \times \Gamma^{(t_N)}$$

- Negative scaling parameter will have meaning in a specific context.

Adiabatic Accessibility

Adiabatic processes

- Adiabatic does not mean slow, quasi-static.
- It only means no ‘heat’ is involved in the state change.
- Adiabatic process can be very violent (e. g. bomb).



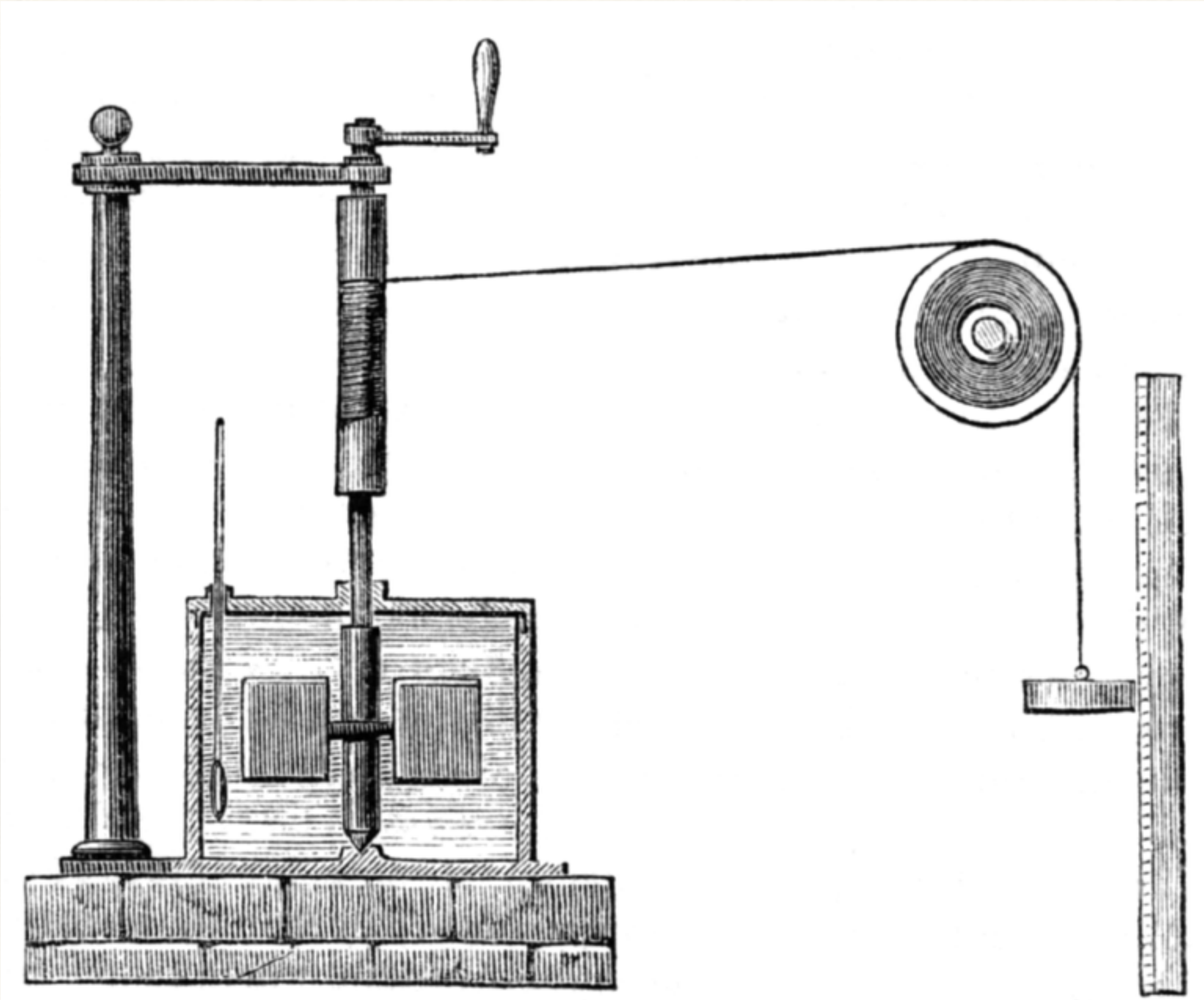
Rubbing is
an adiabatic process.

The Experiments by
Benjamin Thompson

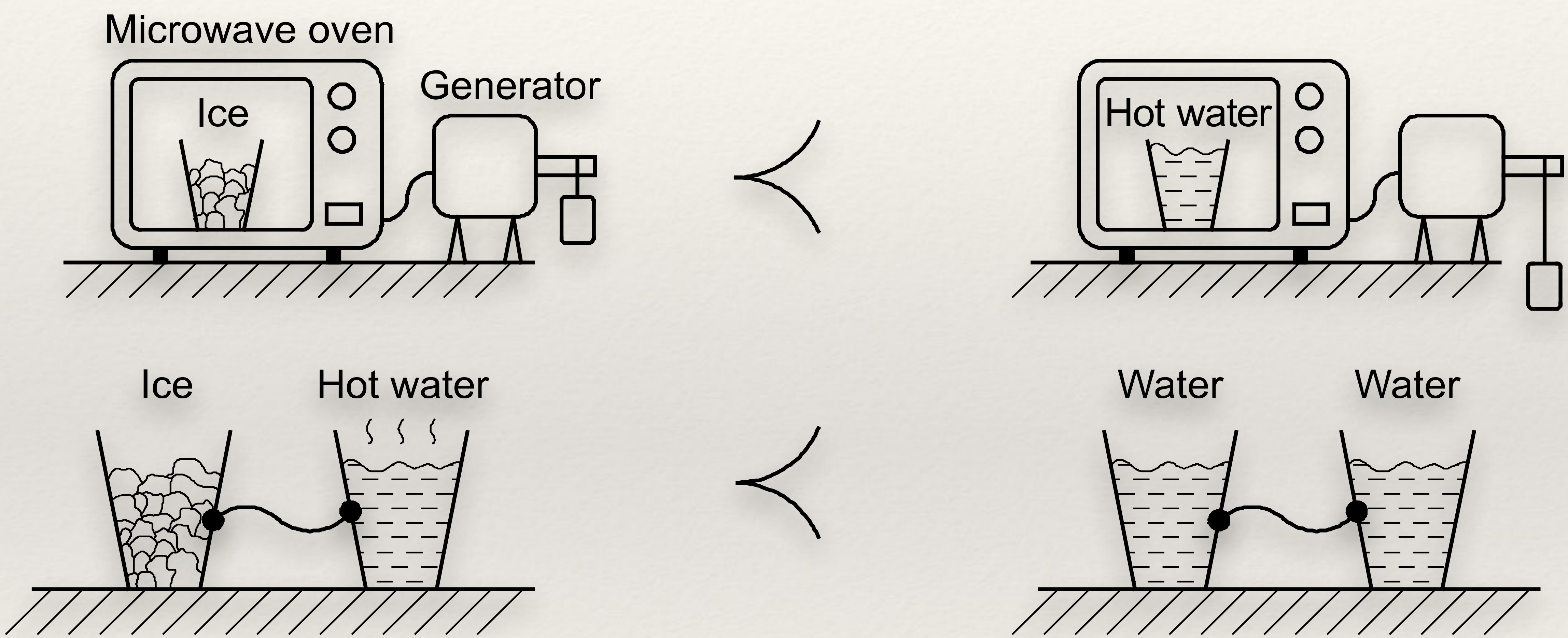
Adiabatic accessibility

A state $\boldsymbol{Y}$ is adiabatically accessible from a state $\boldsymbol{X}$, in symbols $\boldsymbol{X} \prec \boldsymbol{Y}$ (to be pronounced "$\boldsymbol{X}$ precedes $\boldsymbol{Y}$" or "$\boldsymbol{Y}$ succeeds $\boldsymbol{X}$"), if it is possible to change the state from $\boldsymbol{X}$ to $\boldsymbol{Y}$ by means of an interaction with some device (which may consist of mechanical and electrical parts as well as auxiliary thermodynamic systems) and a weight, in such a way that the device returns to its initial state at the end of the process (or can be returned), whereas the weight may have changed its position in a gravitational field.

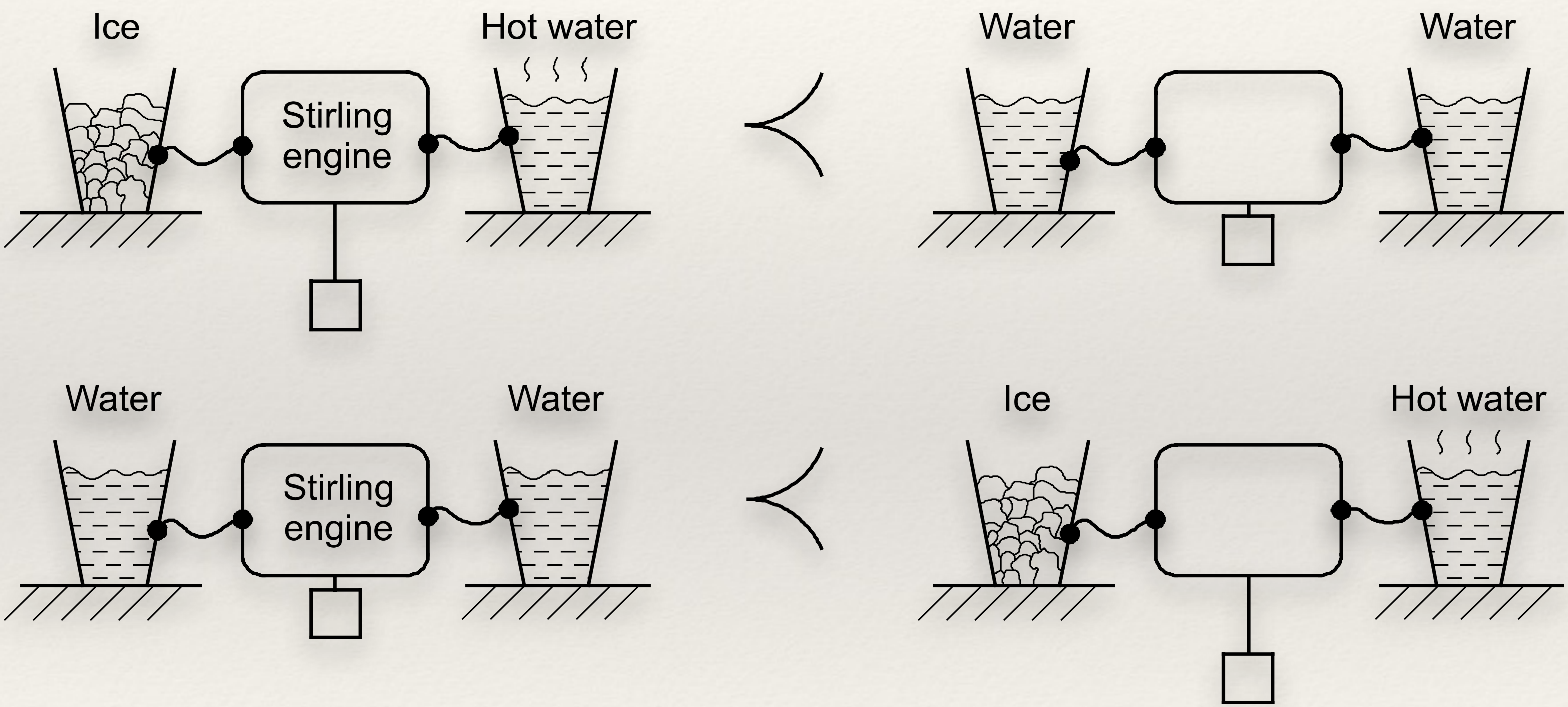
sole results : $X \to Y$ and position change of the weight



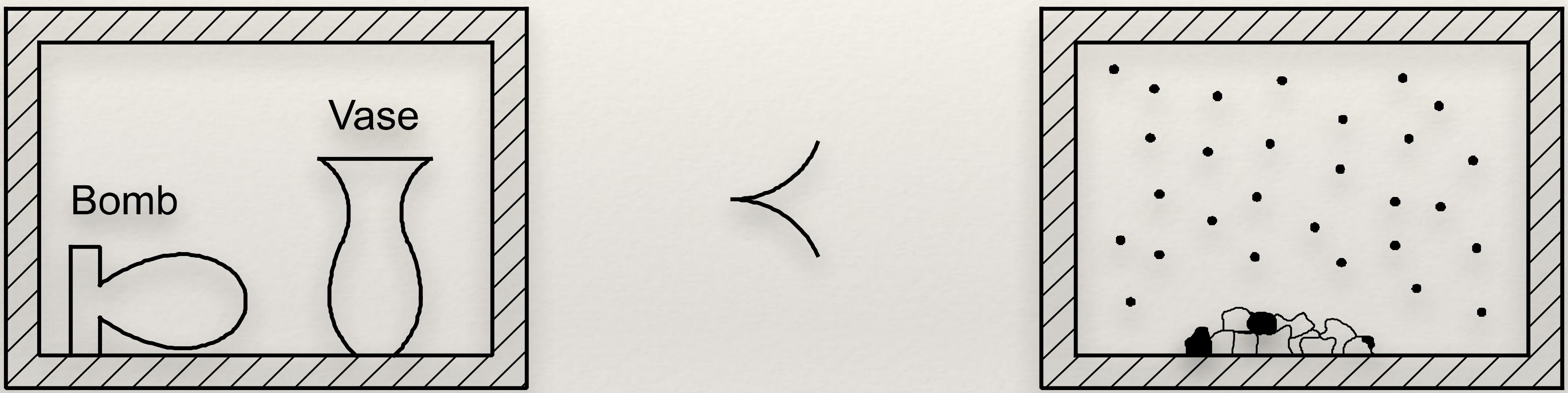
Examples I (from [T])



Examples II (from [T])



Examples III (from [T])



Some notations and terminology

- We write $X \prec\prec Y$ if

$$X \prec Y \text{ but } Y \not\prec X$$

- Comparable if

$$\text{either } X \prec Y \text{ or } Y \prec X$$

- Adiabatically equivalent if ($\prec$ is a *pre*order relation)

$$\text{both } X \prec Y \text{ and } Y \prec X$$

- Adiabatically equivalent states : $X \overset{A}{\sim} Y$

What we want to show

Entropy principle

There is a real-valued function on all states of all systems (including compound systems), called **entropy** *and denoted by S such that*

1. Monotonicity : When X and Y are compable states then

$$X \prec Y \text{ if and only if } S(X) \leq S(Y)$$

2. Additivity and Extensivity : For any X and Y of (possibly different) systems

$$S(X, Y) \equiv S((X, Y)) = S(X) + S(Y)$$
$$S(tX) = tS(X)$$

Remarks

- Monotonicity without comparability

$$X \overset{A}{\sim} Y \Rightarrow S(X) = S(Y),$$
$$X \prec\prec Y \Rightarrow S(X) < S(Y)$$

- Entropy must increase in an “irreversible” process.
- ‘nonequilibrium entropy’?[LY3]
- The aim : What set of axioms is equivalent to the entropy principle?

Remarks

- Entropy also dictates which process is allowed.
- Significance of the additivity in compound systems.

  If $S(X) + S(W) < S(Y) + S(Z), (X, W) \prec (Y, Z)$
- Additivity and extensitivity are independent.

  cf : Cauchy's functional equation
- Photon gas : same entropy for any scaled space.

6 Axioms and Comparison Principle

(A1) Reflexivity. $X \overset{A}{\sim} X$

(A2) Transitivity. $X \prec Y \ \& \ Y \prec Z \Rightarrow X \prec Z$

(A3) Consistency. $X \prec X' \ \& \ Y \prec Y' \Rightarrow (X, Y) \prec (X', Y')$

(A4) Scaling invariance. $X \prec Y \Rightarrow tX \prec tY, \ \forall_{t>0}$

(A5) Splitting and recombination. $For \ 0 < t < 1,$

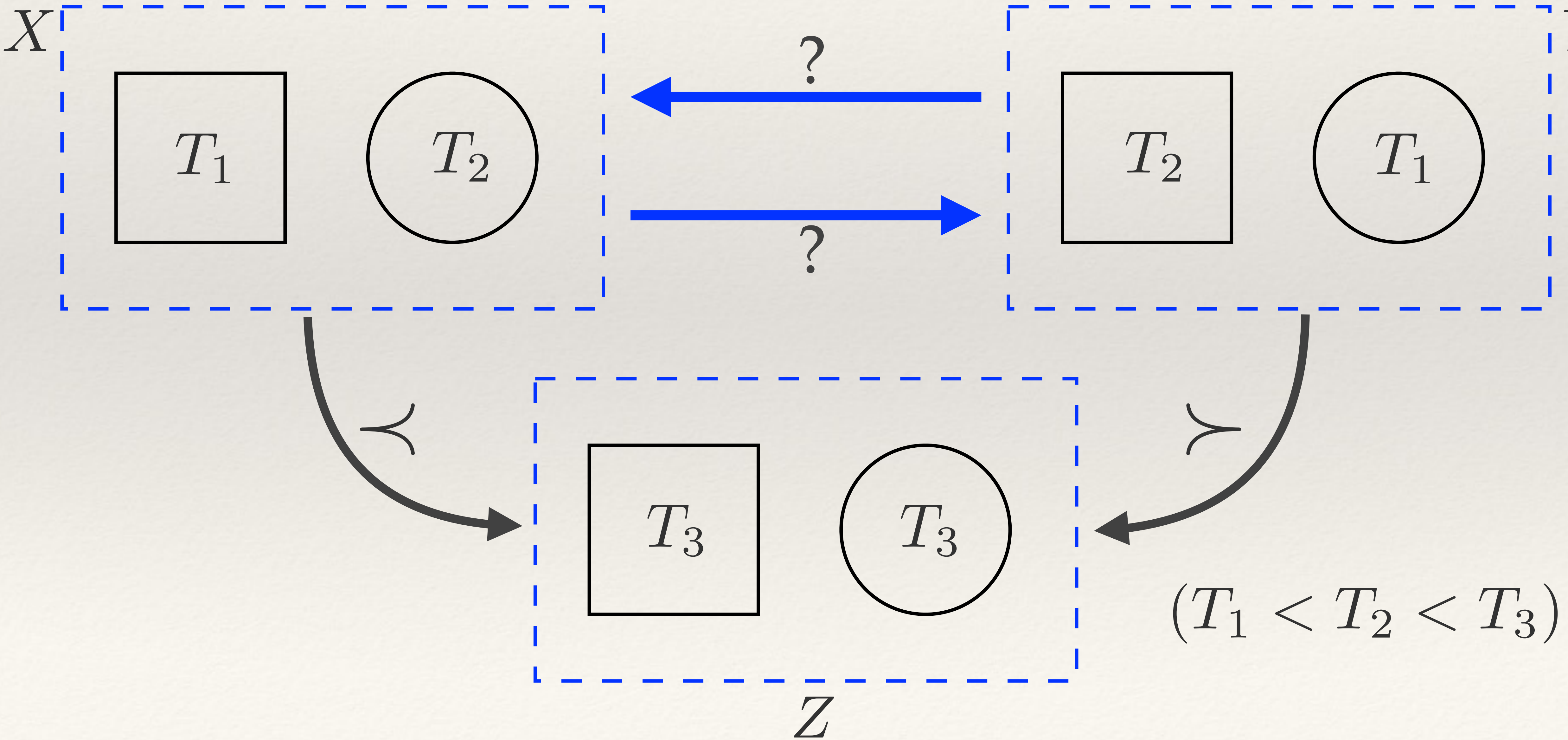
$$X \overset{A}{\sim} (tX, (1-t)X)$$

(A6) Stability. *If* for *some states* Z_0, Z_1 *and for a sequence of* ε*'s, tending to zero,* $(X, \varepsilon Z_0) \prec (Y, \varepsilon Z_1)$ *holds, then*

$$X \prec Y$$

Comparison property (**CP**)

Any two states in a same state space are comparable.



Remarks on **CP**

- Comparability is an equivalence relation.
- It is not *a priori* clear whether the **CP** holds in real physical systems. For example, see page 38 of [B].
- [LY1] proves the **CP** using another set of axioms.
- We shall first find the entropy function for all *scaled products* of a state space Γ.
- The entropy function will turn out to be unique up to an affine transformation. $S(X) \to aS(X) + B$

Mathematical digression: equivalence

- Binary Relation ~ : $x \sim y$
- Examples : 1<2, $A \subset B$
- A relation in a set A is an equivalence relation if
  - it is reflexive ($x \sim x$ for all $x \in A$),
  - it is symmetric ($x \sim y$ implies $y \sim x$),
  - it is transitive ($x \sim y$ and $y \sim z$ implies $x \sim z$).
- Example : 1~3 (modulo 2), 2~4 (modulo 2)

Mathematical digression: equivalence

- An equivalence relation ~ in A partitions the set A by equivalence classes.
- A set of all equivalence classes is called a quotient set and denoted by $A/\sim$.
- Example : The relation modulo 2 divides natural numbers into even and odd numbers.

Stability implies cancellation law

$(X, Z) \prec (Y, Z) \Rightarrow X \prec Y$ (Cancellation Law)

Proof Set $\varepsilon = 1/n$.

$$
\begin{aligned}
(X, \varepsilon Z) &\overset{A}{\sim} ((1-\varepsilon)X, \varepsilon X, \varepsilon Z) && \text{(by } \mathbf{A5}\text{)} \\
&\prec ((1-\varepsilon)X, \varepsilon Y, \varepsilon Z) && \text{(by } \mathbf{A1}, \mathbf{A3}, \text{ and } \mathbf{A4}\text{)} \\
&\overset{A}{\sim} ((1-2\varepsilon)X, \varepsilon X, \varepsilon Y, \varepsilon Z) && \text{(by } \mathbf{A5}\text{)} \\
&\prec ((1-2\varepsilon)X, 2\varepsilon Y, \varepsilon Z) && \text{(by } \mathbf{A1}, \mathbf{A3}\text{–}\mathbf{A5}\text{)} \\
&\prec (Y, \varepsilon Z) && \text{(by repeating)} \quad \blacksquare
\end{aligned}
$$

$$S(X) + S(Z) \leq S(Y) + S(Z) \Rightarrow S(X) \leq S(Y)$$

Construction of Entropy for a Single System

What we want to prove (Thm. 2.2)

There is a function, S_Γ*, on* Γ *with the property that for real numbers satisfying* $t_1 + \cdots + t_N = t'_1 + \cdots + t'_M$ $(N, M \geq 1)$,

$$(t_1 Y_1, \ldots, t_N Y_N) \prec (t'_1 Y'_1, \ldots, t'_M Y'_M)$$

holds if and only if

$$\sum_{i=1}^{N} t_i S_\Gamma(Y_i) \leq \sum_{j=1}^{M} t'_j S_\Gamma(Y'_j).$$

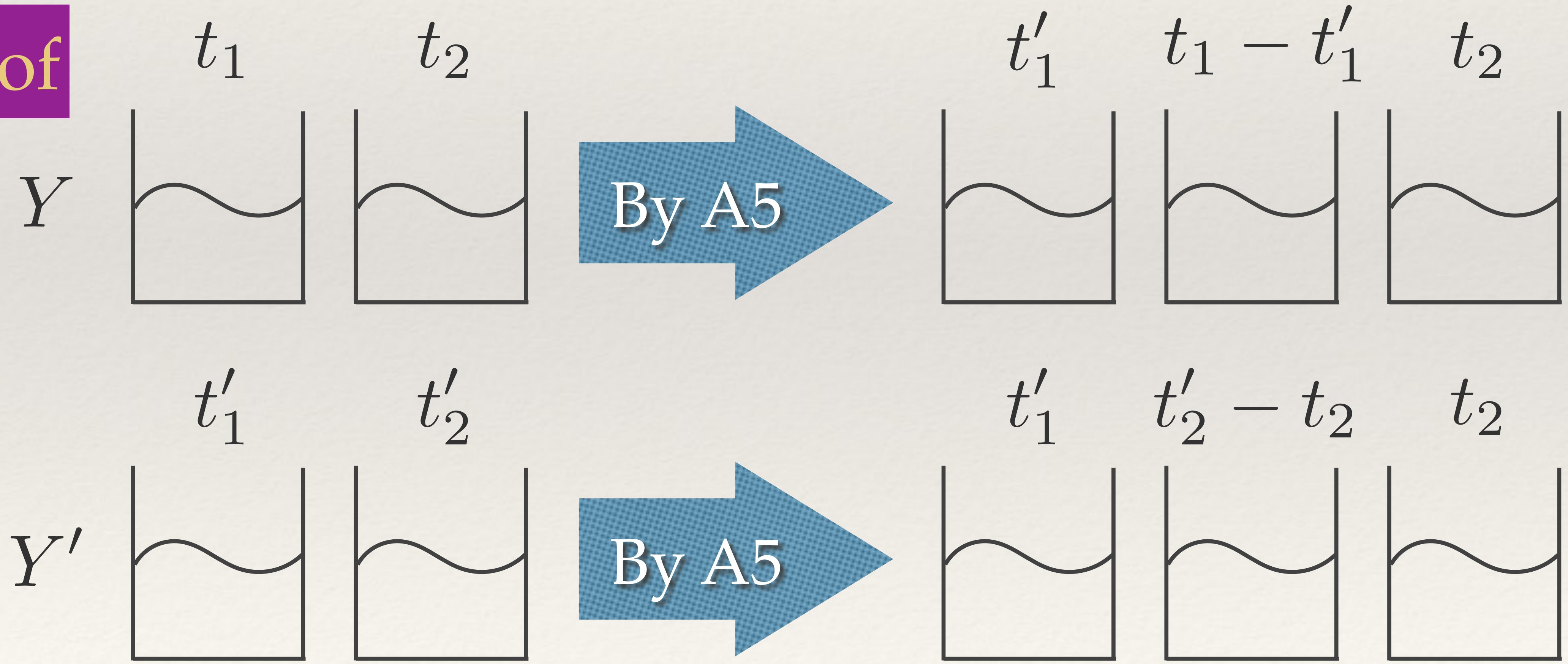
If there is another function S^*_Γ *with the same property, then* $S^*_\Gamma(X) = a S_\Gamma(X) + B$ *with constants* $a > 0$ *and* B*.*

Entropy Constants

CP in multiple scaled copies

Let $Y \in \Gamma^{(t_1)} \times \cdots \times \Gamma^{(t_N)}$ and $Y' \in \Gamma^{(t'_1)} \times \cdots \times \Gamma^{(t'_M)}$.
If **CP** holds in every scaled product space and $\sum_i t_i = \sum_j t'_j$, Y and Y' are comparable.

Proof



■

Generalized ordering

$$(a_1 X_1, \ldots, a_N X_N) \prec (a'_1 X_1, \ldots, a'_M X'_M) \text{ for any } a, a' \in R$$

- When 0, simply ignore it.

$$(0X_1, 2X_2) \prec (2X_3, 0X_4) \text{ means } 2X_2 \prec 2X_3$$

- When negative, move to the other side.

$$(2X_1, X_2) \prec (X_3, -5X_4, X_5) \text{ means } (2X_1, X_2, 5X_4) \prec (X_3, X_5)$$

- **A5** is now extended as follows:

$$X \overset{A}{\sim} (aX, (1-a)X) \ \forall_{a \in R}$$

Lemma 2.1

Suppose X_0 *and* X_1 *are two points in* Γ *with* $X_0 \prec\prec X_1$. *For* $\lambda \in R$ *define*

$$\mathscr{S}_\lambda = \{X \in \Gamma : ((1-\lambda)X_0, \lambda X_1) \prec X\}.$$

Then

(i) *For every* $X \in \Gamma$ *there is a* $\lambda \in R$ *such that* $X \in \mathscr{S}_\lambda$.

(ii) *For every* $X \in \Gamma$, $\sup\{\lambda : X \in \mathscr{S}_\lambda\} < \infty$.

- Canonical entropy function

$$S_\Gamma(X) := \sup\{\lambda : ((1-\lambda)X_0, \lambda X_1) \prec X\}$$

Lemma 2.2 and 2.3

Lemma 2.2 *Suppose* $X_0 \prec\prec X_1$ *are states and* a_0, a_1, a_0', a_1' *are real numbers with* $a_0 + a_1 = a_0' + a_1'$. *Then the following are equivalent.*

(i) $(a_0X_0, a_1X_1) \prec (a_0'X_0, a_1'X_1)$

(ii) $a_1 \leq a_1'$ *(and hence* $a_0 \geq a_0'$*).*

In particular, $\overset{A}{\sim}$ *holds in* (i) *if and only if* $a_1 = a_1'$ *and* $a_0 = a_0'$.

Lemma 2.3 *If* $X \in \Gamma$ *then the equality*

$$\lambda = S_\Gamma(X)$$

is equivalent to

$$X \overset{A}{\sim} ((1-\lambda)X_0, \lambda X_1).$$

Remarks

- By Lemma 2.3 and the cancellation law, the canonical entropy lies between 0 and 1 for a state in a strip [note]

$$\Sigma(X_0, X_1) := \{X \in \Gamma | X_0 \prec X \prec X_1\}$$

- Writing $S_\Gamma(X) = S_\Gamma(X|X_0, X_1)$
- Entropy for states outside the strip $\Sigma(X_0, X_1)$ [note]

$$S_\Gamma(X|X_0, X_1) = S_\Gamma(X_1|X_0, X)^{-1} \text{ if } X_1 \prec X$$

$$S_\Gamma(X|X_0, X_1) = -\frac{S_\Gamma(X_0|X, X_1)}{1 - S_\Gamma(X_0|X, X_1)} \text{ if } X \prec X_0$$

Uniqueness of entropy

If S^*_Γ *is a function on* Γ *that satisfies*

$$((1-\lambda)X, \lambda Y) \prec ((1-\lambda)X', \lambda Y')$$

if and only if

$$(1-\lambda)S^*_\Gamma(X) + \lambda S^*_\Gamma(Y) \leq (1-\lambda)S^*_\Gamma(X') + \lambda S^*_\Gamma(Y'),$$

for all $\lambda \in R$ *and* $X, Y, X', Y' \in \Gamma$, *then*

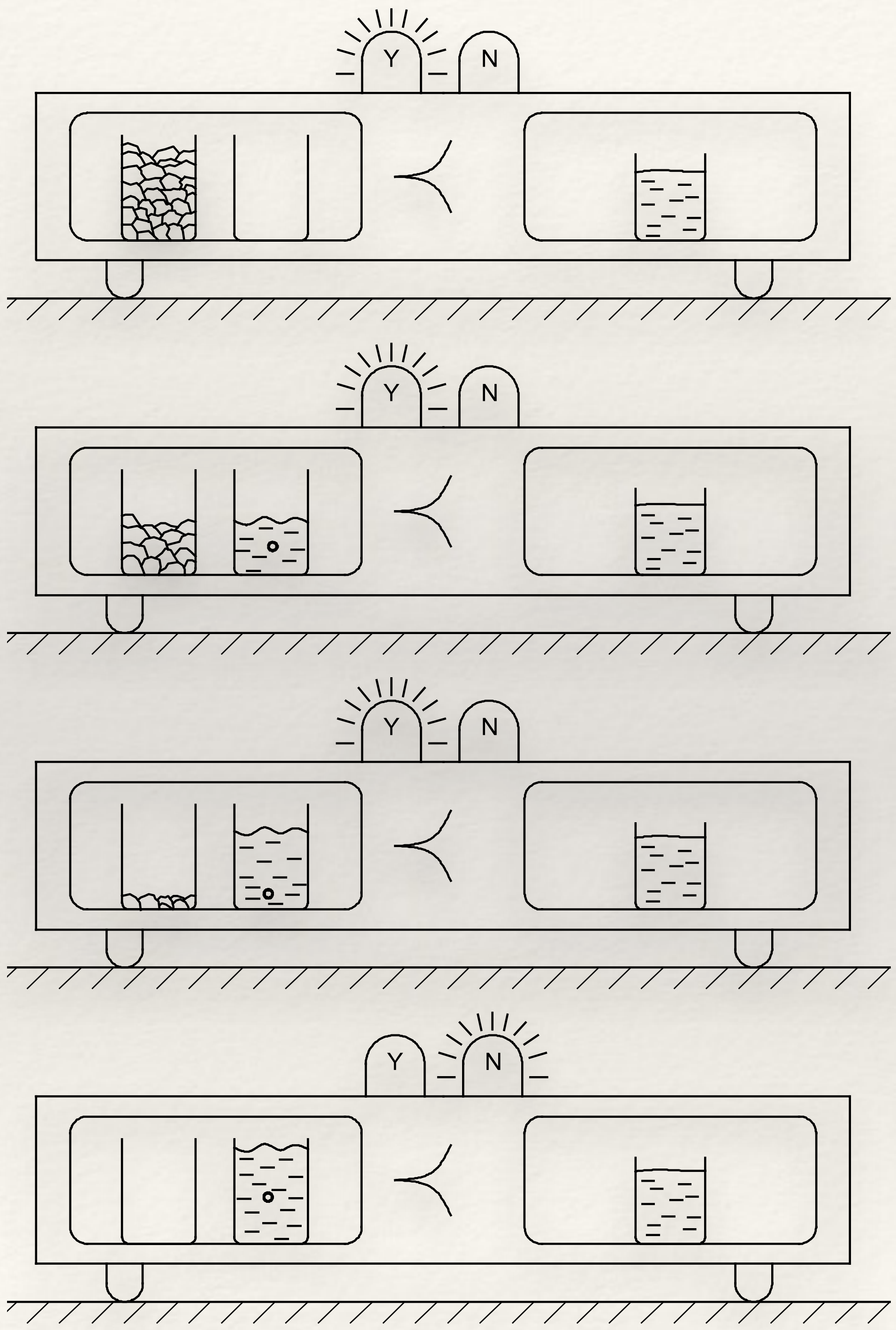
$$S^*_\Gamma(X) = aS_\Gamma(X) + B$$

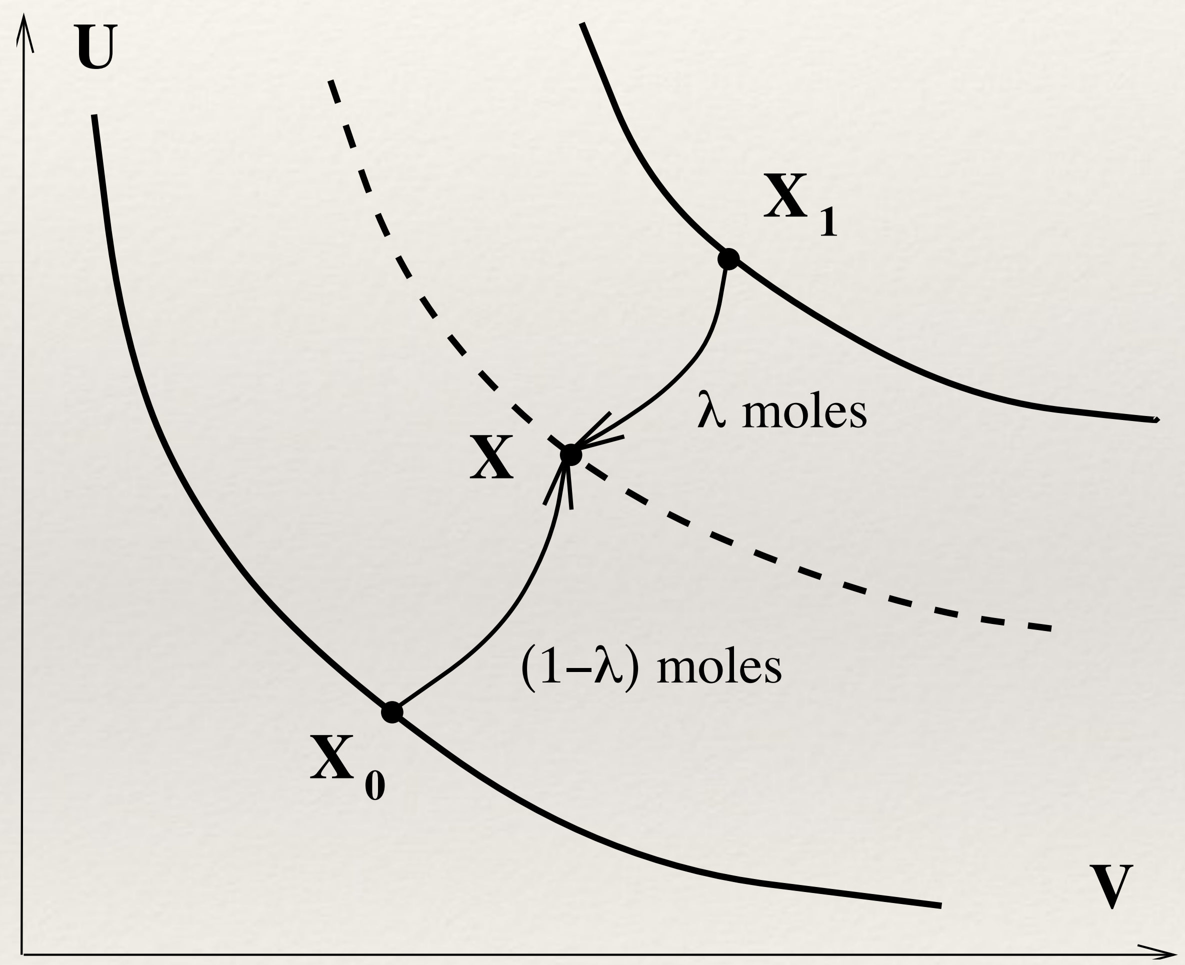
with

$$a = S^*_\Gamma(X_1) - S^*_\Gamma(X_0) > 0, \qquad B = S^*_\Gamma(X_0).$$

Entropy Constants

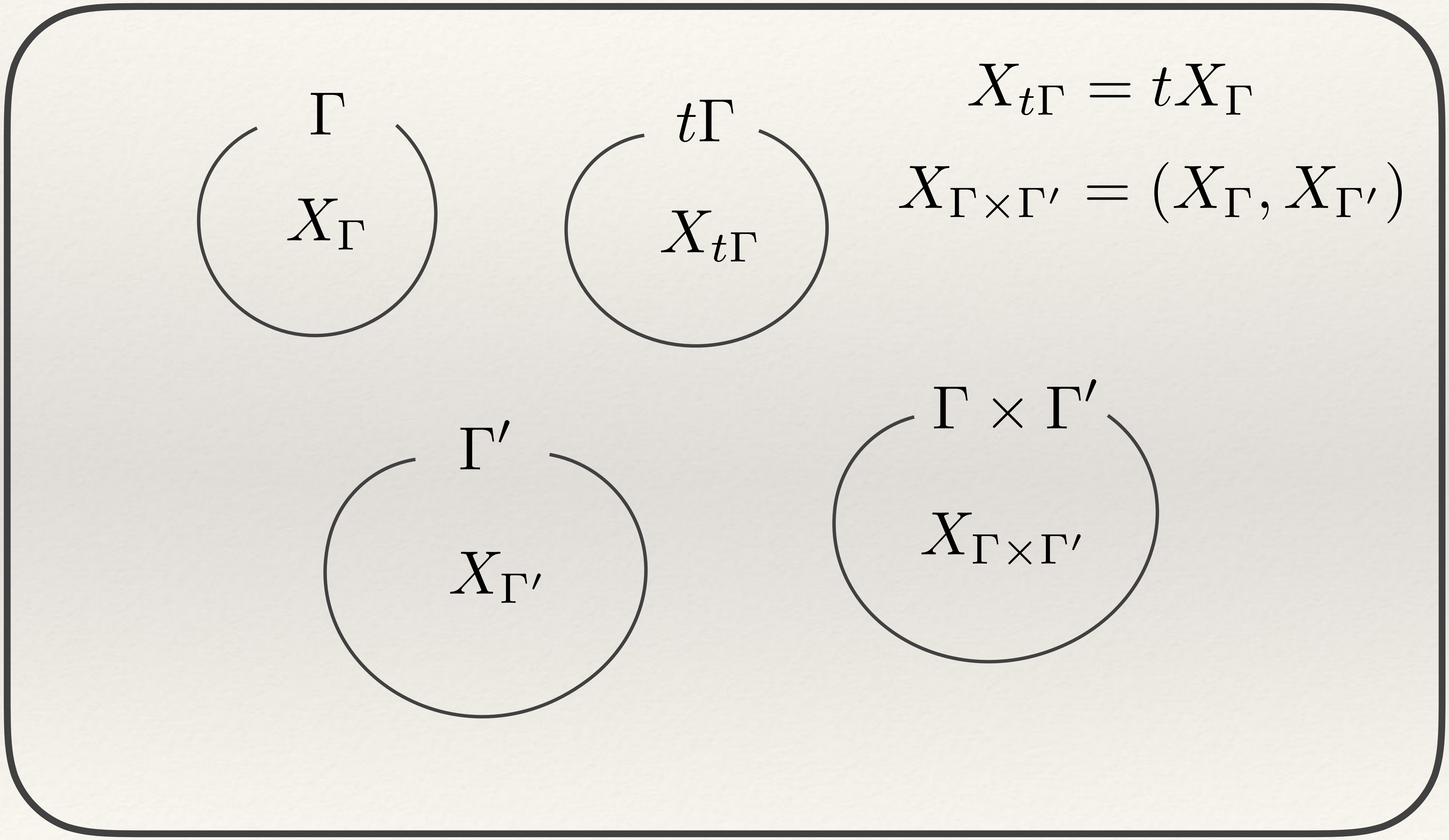
LY machine (from [T])





Constructing Universal Entropy

Consistent entropy scale



Consistent entropy scale

- Fix some system Γ_0 and two point $Z_0 \prec\prec Z_1$ in Γ_0
- For X in Γ, define $S(X)$ as

$$S(X) = S_{\Gamma\times\Gamma_0}((X, Z_0)|(X_\Gamma, Z_0), (X_\Gamma, Z_1))$$

- By previous theorems, we get

$$(X, \lambda Z_0) \overset{A}{\sim} (X_\Gamma, \lambda Z_1)$$

- Due to the choice of X_Γ, we get [note]

$$S(X, Y) = S(X) + S(Y), \quad S(tX) = tS(X)$$

Calibration

- Choose $X_0 \prec\prec X_1 (X_0, X_1 \in \Gamma_0)$
- Choose $Y_0 \in \Gamma$
- Define $S(Y)$ as follows:

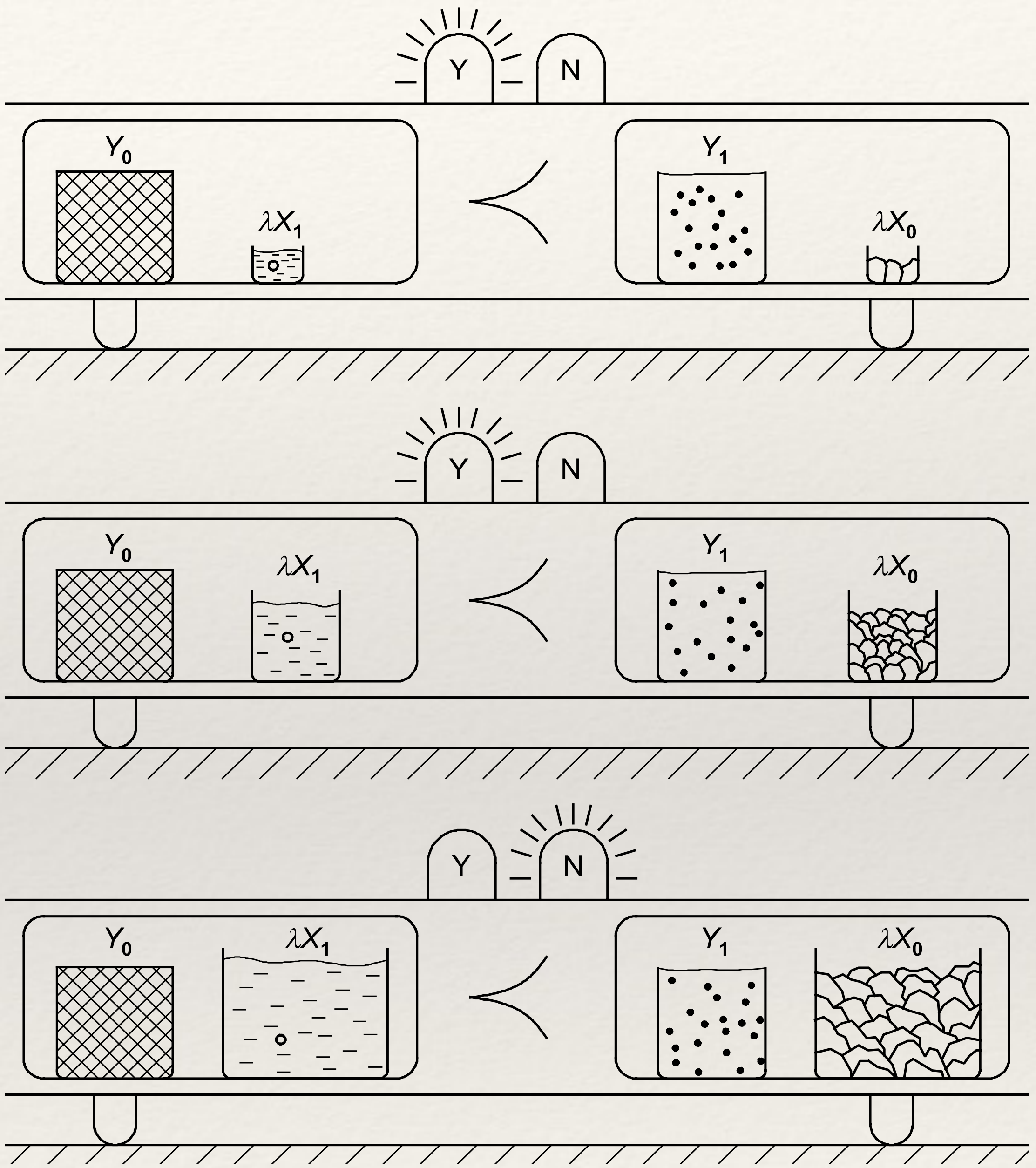
$$S_{\Gamma \times \Gamma_0}((Y, X_0) | (Y_0, X_0), (Y_0, X_1))$$

- By definition,

$$(Y, X_0) \overset{A}{\sim} ((1-\lambda)(Y_0, X_0), \lambda(Y_0, X_1))$$

- By A5 and the cancellation law,

$$(Y, \lambda X_0) \overset{A}{\sim} (Y_0, \lambda X_1)$$



$$S(Y_1) - S(Y_0) = \lambda(S(X_1) - S(X_0))$$

In words,

We can "extract" a desired amount of entropy from X_1 and "inject" it into Y_0 in order to measure by how much the entropy of the latter system increases.

–*Thess*

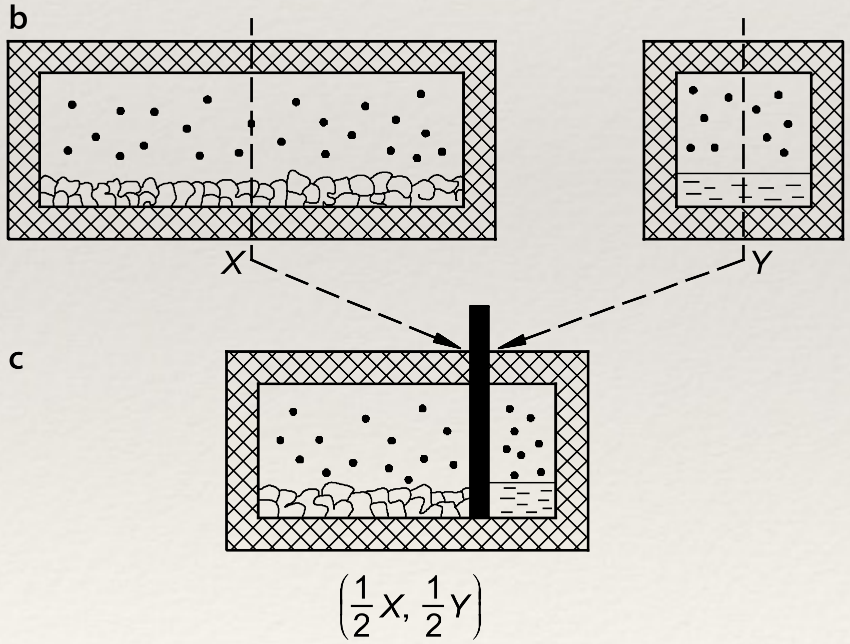
Concavity of Entropy

Convex state space

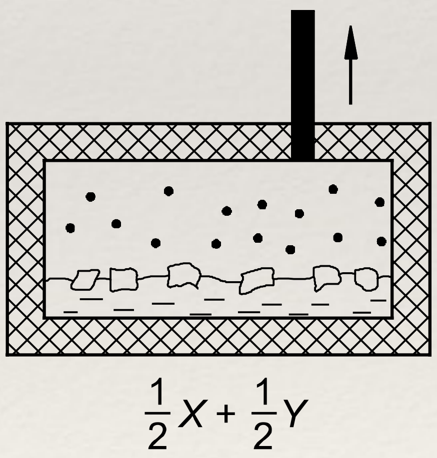
- Convex combination is a well-defined point in the space

$$tX + (1 - t)Y, \text{ where } 0 \le t \le 1$$

- Coordinates should be *U, V* rather than *T, P* and so on.



Compound system



Convex combination

What we want to prove

- ***Entropy is a concave function of states.***

$$S(tX + (1-t)Y) \geq tS(X) + (1-t)S(Y)$$

- Remarks
  - Concavity will be used to define temperature.
  - Maximum entropy principle will be proven.

(A7) Convex combination

- **(A7)** *For X, Y in a convex state space,*

$$(tX, (1-t)Y) \prec tX + (1-t)Y$$

- **Forward sector** of $X \in \Gamma$ in Γ

$$A_X := \{Y \in \Gamma | X \prec Y\}$$

- **Forward sector** of $X \in \Gamma$ in another system Γ'

$$\{Y \in \Gamma' | X \prec Y\}$$

Forward sectors are convex

Proof Suppose $X \prec Y_1, X \prec Y_2,$ where $X \in \Gamma, Y_i \in \Gamma'$.

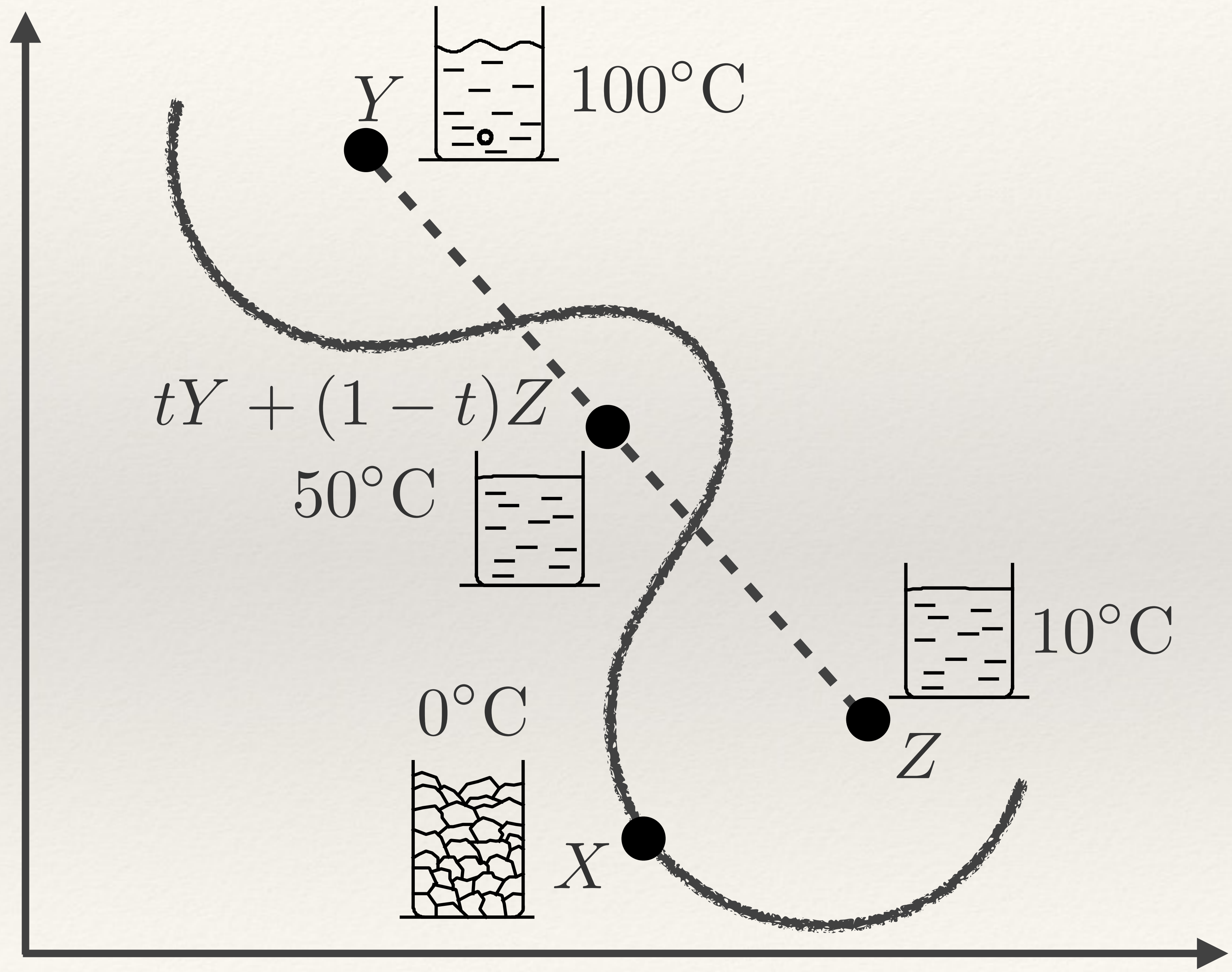
$$\begin{aligned} X &\overset{A}{\sim} (tX, (1-t)X) && \text{(by } \mathbf{A5}\text{)} \\ &\prec (tY_1, (1-t)Y_2) && \text{(by } \mathbf{A3} \text{ and } \mathbf{A4}\text{)} \\ &\prec tY_1 + (1-t)Y_2 && \text{(by } \mathbf{A7}\text{)} \end{aligned}$$

Thus, $X \prec tY_1 + (1-t)Y_2$ by **A2** ■

Corollary $\mathscr{S}_\lambda = \{X : ((1-\lambda)X_0, \lambda X_1) \prec X\}$ is convex.

Thm 2.7 $X \in \mathscr{S}_{\lambda_1},\ Y \in \mathscr{S}_{\lambda_2} \Rightarrow tX + (1-t)Y \in \mathscr{S}_\lambda,$
where $\lambda = t\lambda_1 + (1-t)\lambda_2$ [note]

Why we need convexity



Concavity of entropy

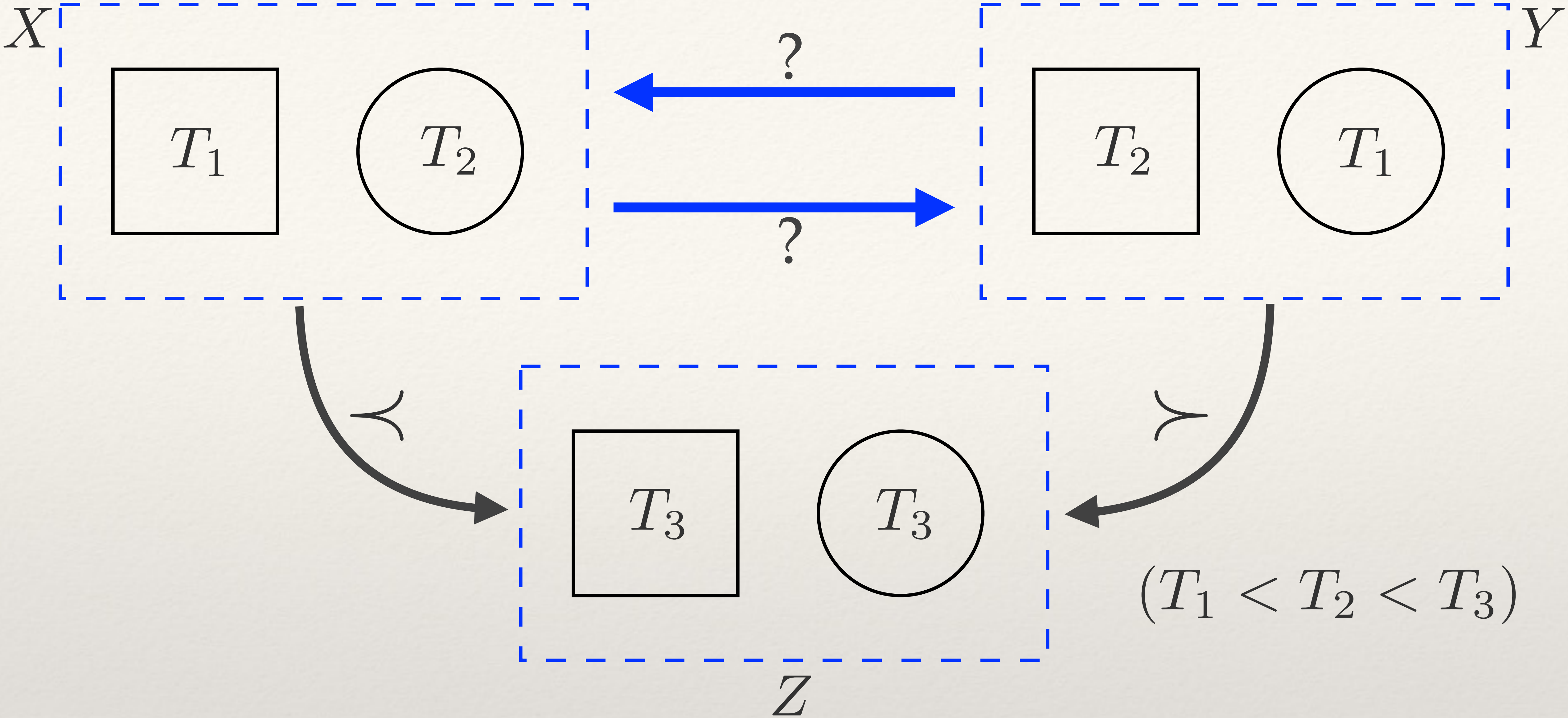
- **Thm 2.8** The canonical entropy is a concave function. Conversely, if an entropy is concave, then axiom A7 necessarily holds *a fortiori*.

Proof Choose $S(X) = \lambda_1, S(Y) = \lambda_2$.

By Thm 2.7 , $tX + (1-t)Y \in \mathscr{S}_\lambda$. Thus,

$$
\begin{aligned}
S(tX + (1-t)Y) &\geq \lambda = t\lambda_1 + (1-t)\lambda_2 \\
&= tS(X) + (1-t)S(Y)
\end{aligned}
$$

■



Comparison Principle

Simple Systems

Thermal Equilibrium

Compound Systems

Internal Energy and Coordinates

Measurability of Energy

- Hamiltonian dynamics is gauge invariant. [note]
- An essential prerequisite for the measurability of the energy is *the existence of wall that do not permit the transfer of energy in the form of heat*. [C]
- We conclude that we are able to measure the energy difference of two states *provided that one state can be reached from the other by some mechanical process while the system is enclosed by an adiabatic impermeable wall.* [C]

Axiomatic Approach [B]

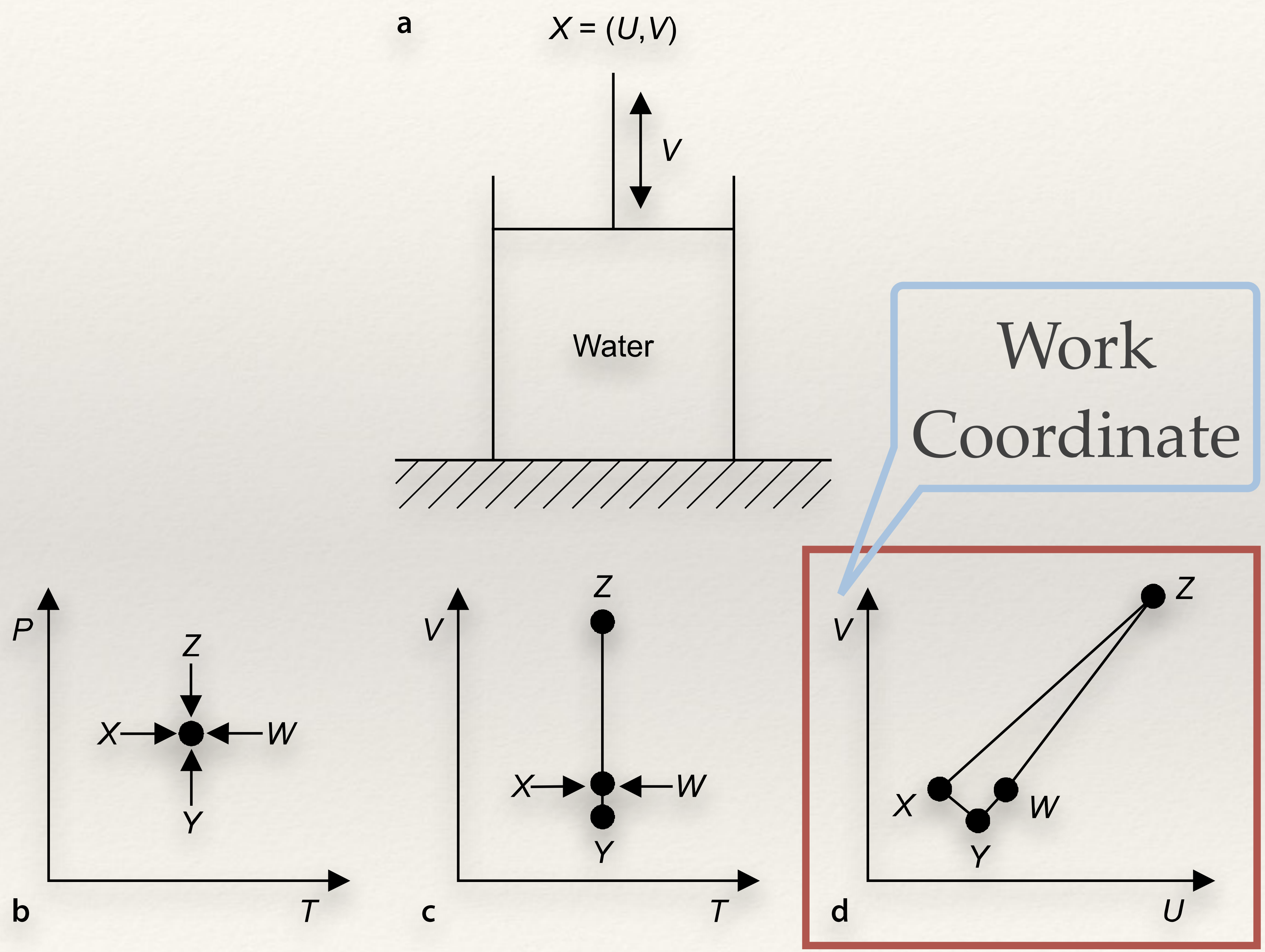
- **Existence of work function**. If $X \prec Y$, there is a unique real number $W(X,Y)$ (work done by the system).
- **The 1st law of thermodynamics**. If $X \prec Y$ and $Y \prec Z$,

$$W(X,Z) = W(X,Y) + W(Y,Z)$$

- Theorem : There exists a real-valued function U (to be called internal energy) on Γ with the property

$$W(X,Y) = U(X) - U(Y) \text{ whenever } X \prec Y$$

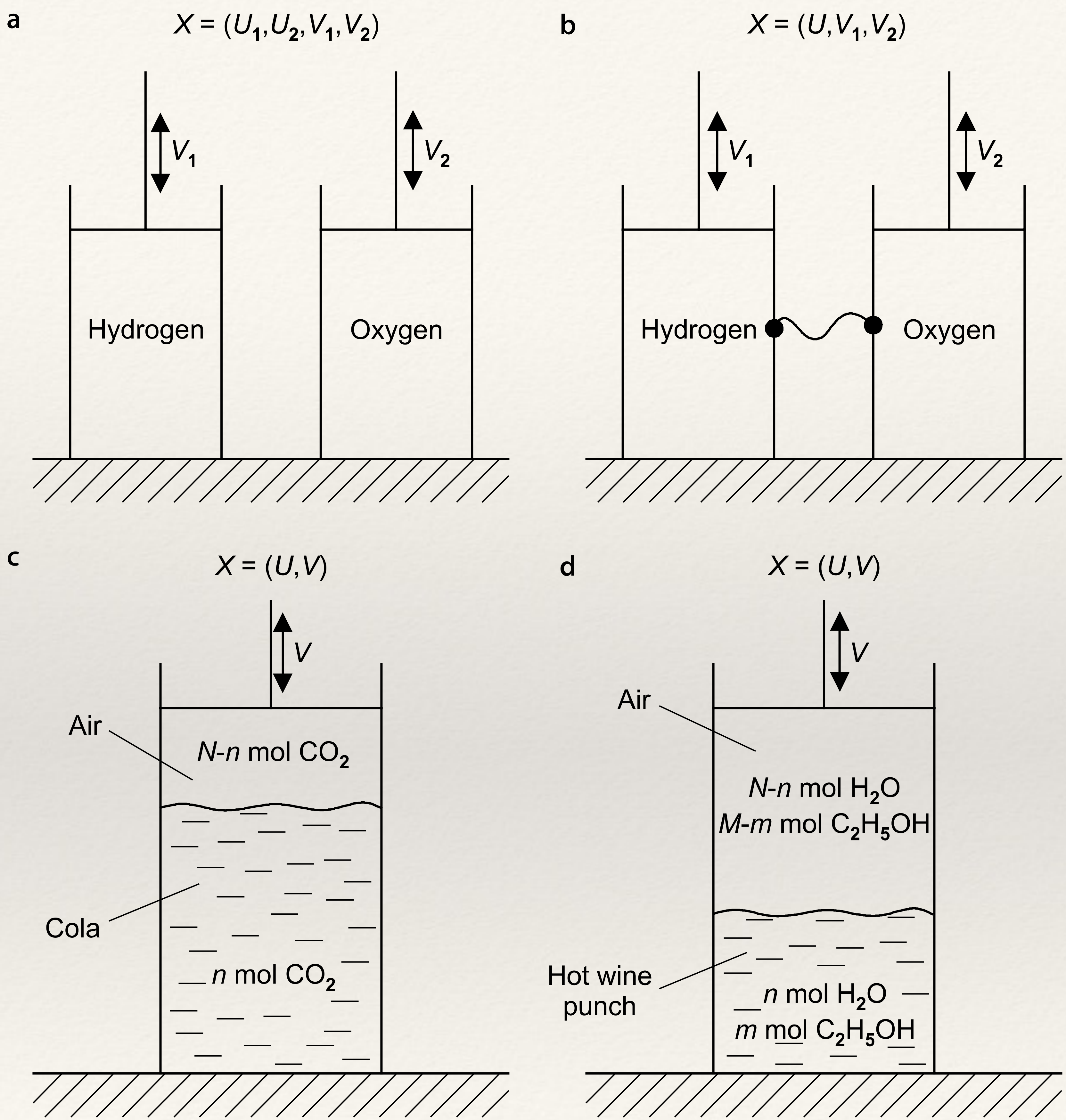
Macroscopic coordinates



3 Axioms for Simple Systems

Remarks on simple systems

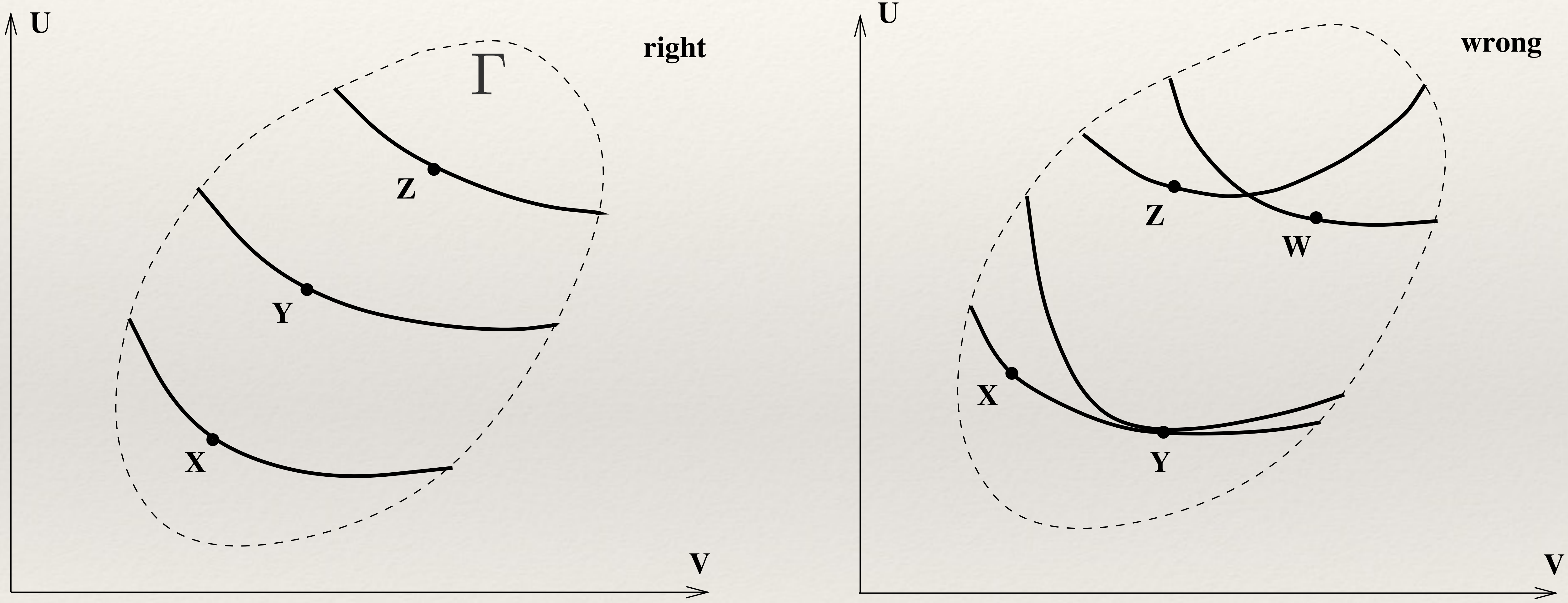
- One (internal) energy and n work coordinates.
- Spatially inhomogeneous simple system.
- Energy and volume are fundamental as coordinates.
- A state is a point in $\mathbf{R}^{n+1}$ and $\Gamma \subset \mathbf{R}^{n+1}$.
- A **thermometer** or **degenerate simple system:** $n = 0$.
- Although $\Gamma^{(t)} \subset \mathbf{R}^{n+1}$, Γ and $\Gamma^{(t)}$ should be considered completely different spaces (exception : photon gas).



a
X = (U1,U2,V1,V2)
V1
V2
Hydrogen
Oxygen
b
X = (U,V1,V2)
V1
V2
Hydrogen
Oxygen
c
X = (U,V)
V
Air
N-n mol CO2
Cola
n mol CO2
d
X = (U,V)
V
Air
N-n mol H2O
M-m mol C2H5OH
Hot wine punch
n mol H2O
m mol C2H5OH

What to prove

- In simple systems, forward sectors are nested.



- Accordingly, the **CP** holds within the state spaces of simple systems.

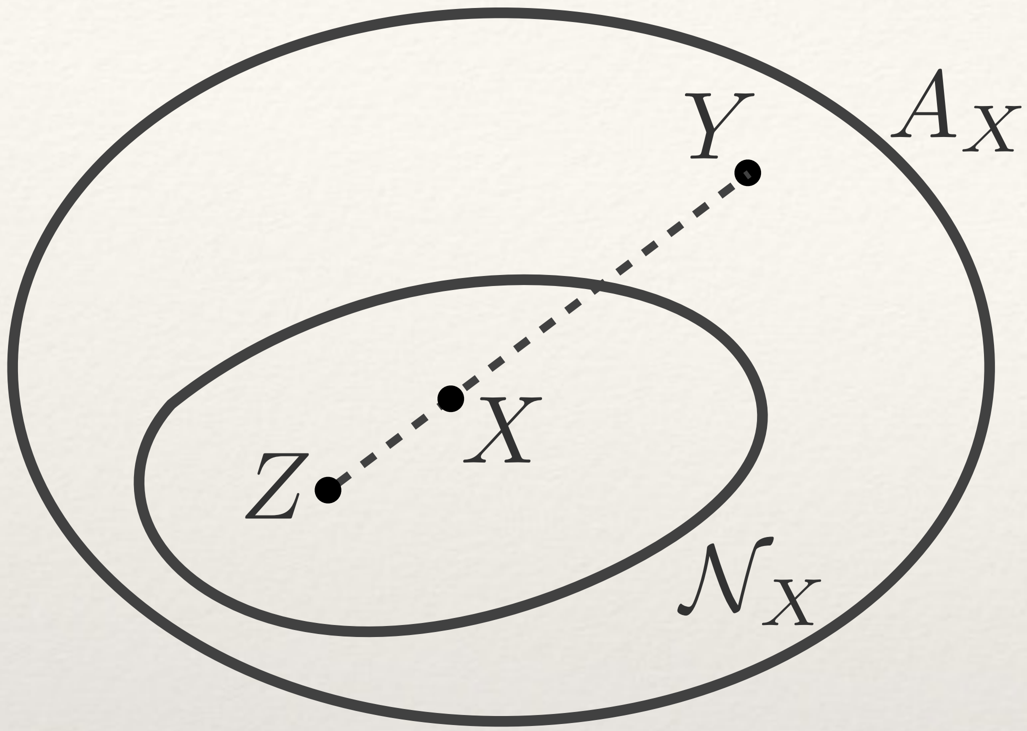
Axioms

- **(S1) Irreversibility.** For each state $X \in \Gamma$, there is another state $Y \in \Gamma$ such that $X \prec\prec Y$
- **(S2) Lipschitz tangent planes.** For each $X \in \Gamma$ the forward sector A_X has a unique support plane at X, denoted by Π_X, which is assumed to have a finite slope w.r.t. the work coordinates and the slope is moreover assumed to be a locally Lipschitz continuous function of X.
- **(S3) Connectedness of the boundary**. ∂A_X is arcwise connected.

(S1) Irreversibility

- ***For each state*** $X \in \Gamma$***, there is another state*** $Y \in \Gamma$ ***such that*** $X \prec\prec Y$.
- Carathéodory Principle (**Ca**) : In every neighborhood of every state $X \in \Gamma$, there is a state $Z \in \Gamma$ such that $X \stackrel{A}{\sim} Z$ is false. Here, axioms A1~A7 are assumed to hold.
  1. **S1** always implies **Ca**.
  2. If all the forward sectors have non-empty interiors then **Ca** implies **S1**.

Assume **Ca** is false.



$$((1-\lambda)Z, \lambda Y) \prec X \quad \text{(by } \mathbf{A7}\text{)}$$

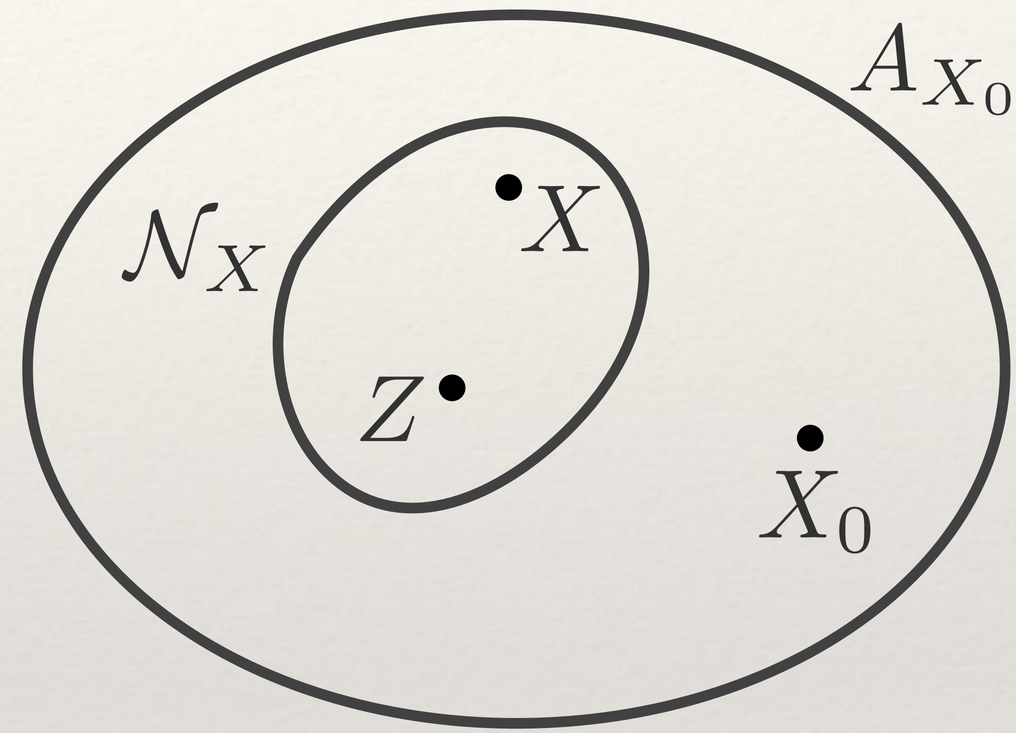
$$\overset{A}{\sim} ((1-\lambda)X, \lambda X) \quad \text{(by } \mathbf{A5}\text{)}$$

$$\prec ((1-\lambda)Z, \lambda X) \quad \text{(by Assump)}$$

$$\therefore Y \prec X. \ \mathbf{S1} \text{ is false}$$

Assume **S1** is false.

$$\exists_{X_0} A_{X_0} = \{Y | X_0 \overset{A}{\sim} Y\}$$



There is an interior point X

By transitivity of $\overset{A}{\sim}$

Ca is false.

Remarks

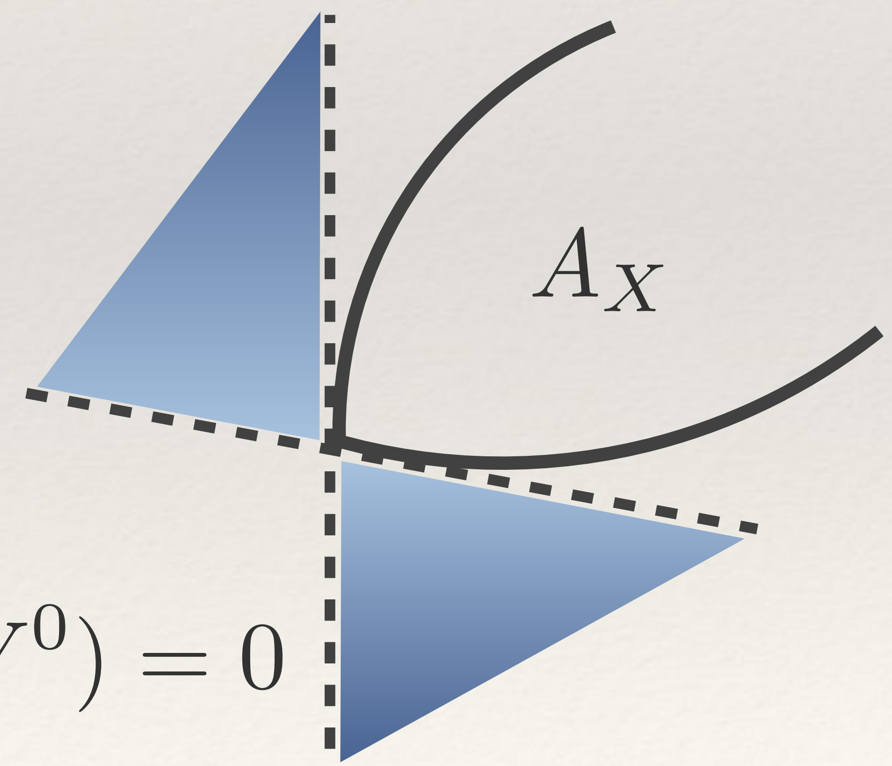
- **Ca** is replaced by **S1**.
- Any state is a boundary point of its forward sector, i.e.,

$$X \in \partial A_X$$

- Since A_X is convex, there is at least one *support plane* which passes through X and of which A_X lies entirely on one side.
- Next axiom is about this support plane.

(S2) Lipschitz tangent planes

- ***For each $X \in \Gamma$ the forward sector A_X has a <u>unique</u> support plane at X, denoted by Π_X, which is assumed to <u>have a finite slope w.r.t. the work coordinates</u> and the slope is moreover assumed to be a locally Lipschitz continuous function of X.***



- It assumes no cusp at X.
- Tangent plane is a linear equation.

$$U - U^0 + \sum_{i=1}^{n} P_i(X)(V_i - V^0) = 0$$

Uniqueness of the support plane

- Mathematical meaning:

  $\varphi(X) = U - U_0 + \sum_i g_i(V - V_0)$ has a unique sign for all $X \in A_X$ if and only if $g_i = P_i(X)$.

- Function $X \mapsto P(X) = (P_1(X), \cdots, P_n(X))$ is called the **pressure**. We do not need to assume $P_i(X) \geq 0$.

- Finite pressure means the plane is never 'vertical'.

Local Lipschitz continuity

- Mathematical definition. For any closed ball B with finite radius, there is a constant $c(B)$ such that

$$|P_i(X) - P_i(Y)| \leq c(B)|X - Y|, \quad \forall_{X,Y \in B}$$

- Rademacher's Thm: a locally Lipschitz continuous function is *differentiable* *almost everywhere*. [note]
- Note that at phase transition points, pressure may be non-differentiable.

(S3) Connectedness of boundary

- ∂A_X ***is assumed to be arcwise connected***.
- Physical motivation : Any two states on the boundary can be reachable each other by a quasi-static process.
- Without **S3**, one can build a model violating the **CH**.
- **Adiabats** : a set of boundaries $\{A_X\}_{X \in \Gamma}$
- Later, we will show $X \in \partial A_Y$ implies $Y \in \partial A_X$

Geometry of Forward Sectors

Mathematical digression: topology

- Open and closed sets. Interior and boundary.
- Closure : the smallest closed set containing a set A.
- Open covering : a set of open sets covering a set A.
- Relative topology
- Compact set : finite open covering.
- Heine-Borel theorem : compact = closed and bounded in Euclidean space.

Lemma 3.1 (collinear points)

- Let $Y = tX + (1-t)Z, \quad t \in [0,1]$

1. If $X \prec Z$, then $X \prec Y$.

   Proof $X \prec (tX, (1-t)X) \prec (tX, (1-t)Z) \prec Y$ ■

2. If $Y \prec Z$, then $X \prec Y$ (and hence $X \prec Z$)

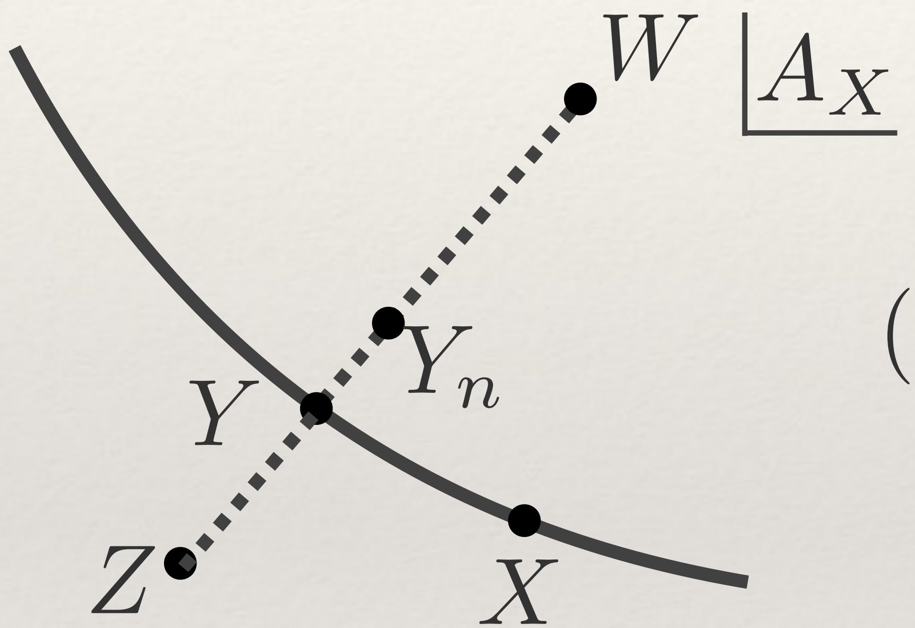
   Proof

$$(tX, (1-t)Z) \prec Y \prec (tY, (1-t)Y) \prec (tY, (1-t)Z)$$ ■

Forward sectors are closed

- *If* $Y \in \partial A_X$, then $Y \in A_X$

Proof



$$\frac{n}{n+1} Y_n + \frac{1}{n+1} Z = Y$$

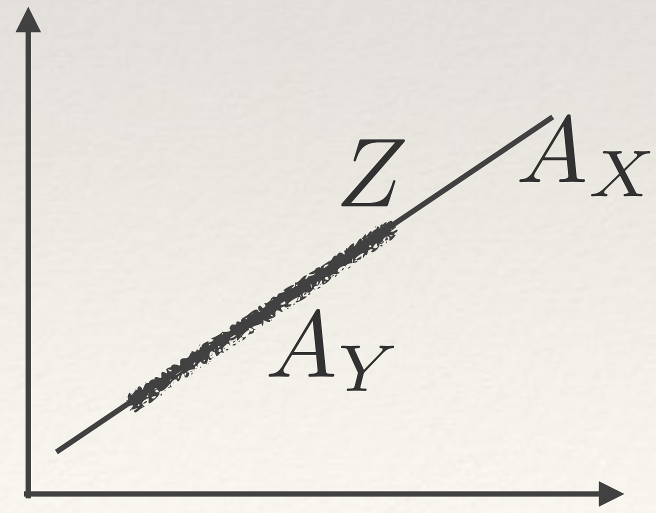
$$(Y_n, \frac{1}{n} Z) \prec \frac{n+1}{n} Y \prec (Y, \frac{1}{n} Y)$$

Since $X \prec Y_n$, $X \prec Y$ ■

- We have only used **A1—A7**.

Forward sectors have interiors

- Note
  - A convex set either has an interior or belongs to a hyperplane in lower dimensions.
  - If Z is a bdy point of a forward sector immersed in a hyperplane, there are many supporting planes at Z.
- Sketch of Pf.



By **S1**, $\exists_Y X \prec\prec Y$

$A_Y \subset A_X \& A_X \neq A_Y$

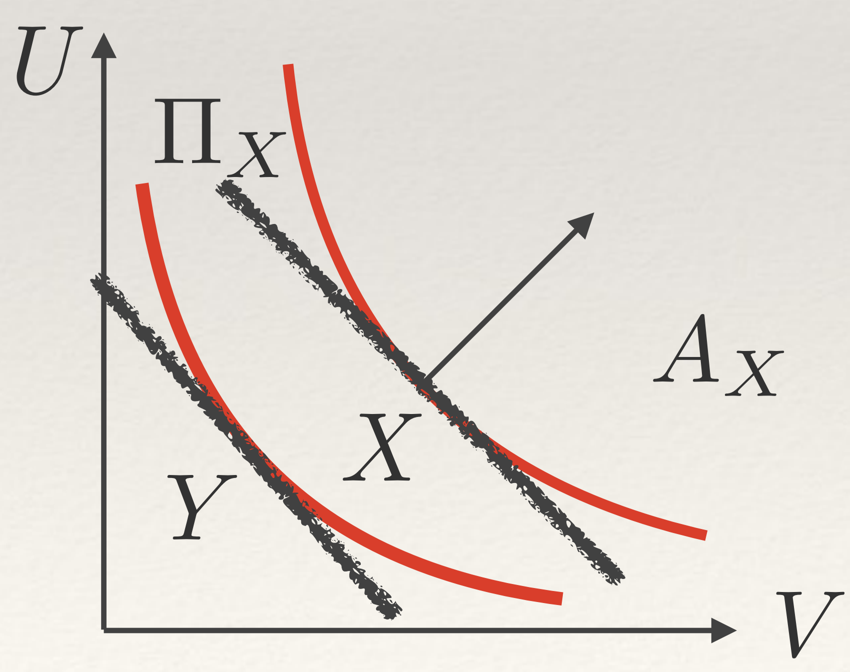
If $Z \in \partial A_Y$ **S2** is false.

Remarks

- It makes sense to talk about the normal direction of a tangent plane, pointing to the interior.
- By S2, the normal is not orthogonal to the energy axis.
- **Thm 3.3**. the normal is continuous on X.
- The normal is set to be on the positive energy side. This will be true for all systems (**Thm 4.2**)
- Temperature is always positive. Negative temperature?

Energy in forward sectors

- If A_X is on the positive energy side of Π_X, $[X = (U_0, V_0)]$ then $A_X \cap \{(U, V_0) | U \in \mathbf{R}\} = \{(U, V_0) : U \geq U_0\} \cap \Gamma$
- If A_X is on the positive energy side of Π_X, then the same holds for all states.

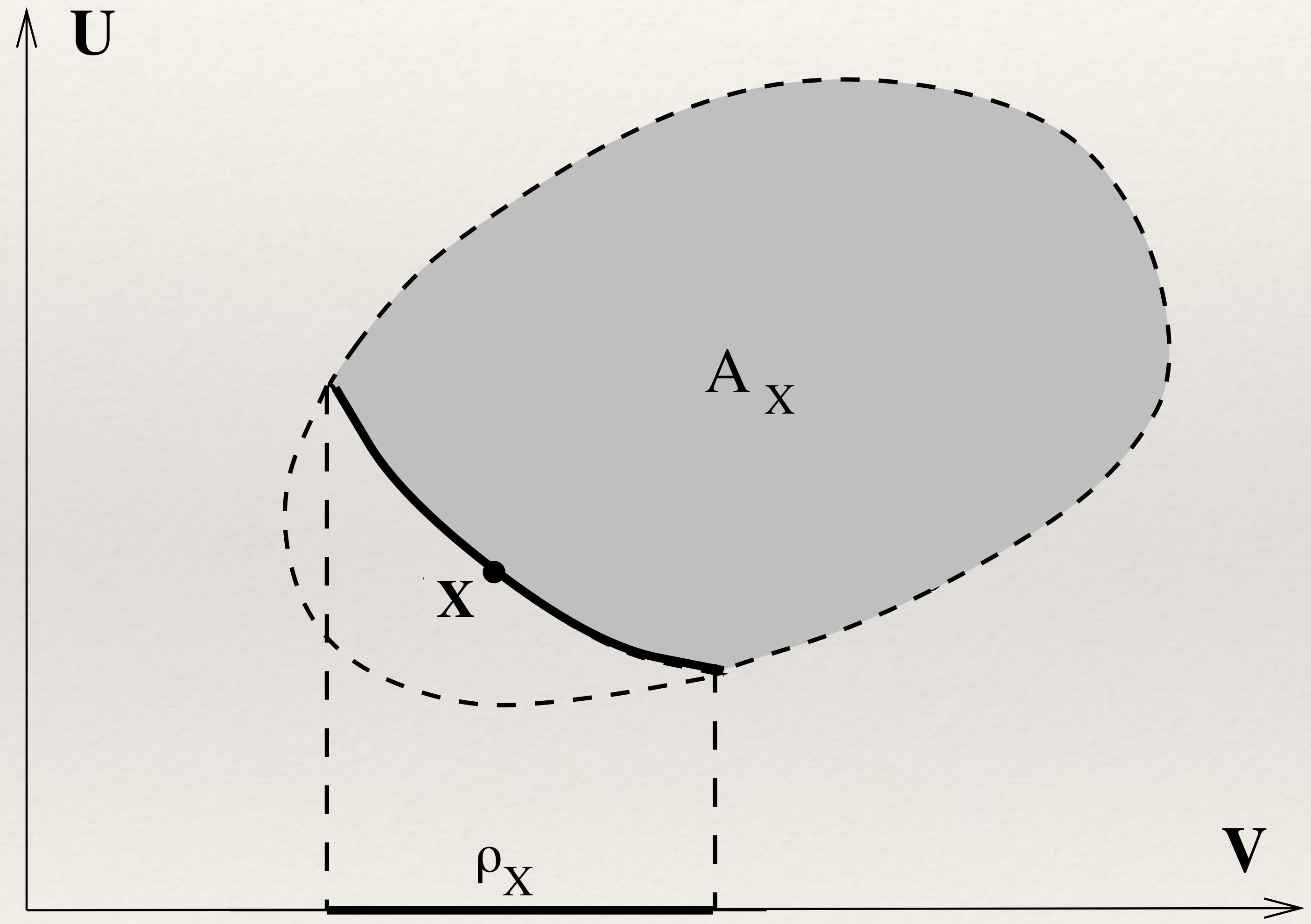


Planck's principle (Thm. 3.4)

- ***If two states of a simple system have the same work coordinates, then*** $X \prec Y \Leftrightarrow U(X) \leq U(Y)$
- $U(X)$ is the energy of the state X.
- 'only if' part is the Kelvin-Planck statement: "*No process is possible, the sole result of which is a change in the energy of a simple system (without changing the work coordinates) and the raising of a weight*"
- Planck's principle is not enough to show the **CP**.

Projection of boundary

$$\rho_X := \{V \in R^n : (U, V) \in \partial A_X \text{ for some } U \in R\}$$



connected by **S3**

Properties of boundaries

(i) *If* $Y \in \partial A_X$, A_X *has a tangent plane at* Y, *which is* Π_Y.

(ii) ρ_X *is an open, connected subset of* R^n.

(iii) *For each* $V \in \rho_X$ *there is exactly one number,* $u_X(V)$, *such that* $(u_X(V), V) \in \partial A_X$. *I.e.,*

$$\partial A_X = \{(u_X(V), V) : V \in \rho_X\}.$$

This $u_X(V)$ *is given by* $u_X(V) = \inf\{u : (u, V) \in A_X\}$. *The function* u_X *is continuous on* ρ_X *and locally convex, i.e.,* u_X *is convex on any convex subset of* ρ_X. *Moreover,*

$$A_X \supset \{(U, V) : U \geq u_X(V), \quad V \in \rho_X\} \cap \Gamma.$$

Properties of boundaries

(iv) *The function u_X is a differentiable function on ρ_X with a locally Lipschitz continuous derivative and satisfies the system of partial differential equations*

$$\frac{\partial u_X}{\partial V_j}(V) = -P_j(u_X(V), V) \quad \text{for } j = 1, \ldots, n \ .$$

(v) *The function u_X is the only continuous function defined on ρ_X that satisfies the above differential equation in the sense of distributions, and that satisfies $u_X(V^0) = U^0$.*

(vi) *If $Y \in \partial A_X$, then $X \in \partial A_Y$ and hence $A_X = A_Y$.*

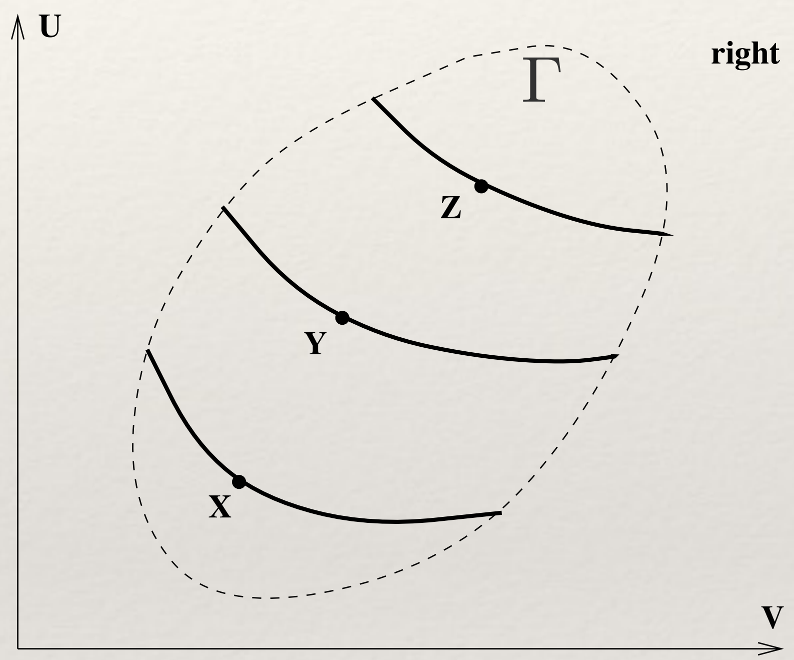
Forward Sectors are nested

- Two forward sectors satisfy exactly one of 3 possibilities.

(a) $A_X = A_Y, \; i.e., \; X \overset{A}{\sim} Y$

(b) $A_X \subset \text{Interior} A_Y, \; i.e., \; X \prec\prec Y$

(c) $A_Y \subset \text{Interior} A_X, \; i.e., \; Y \prec\prec X$



- Hence, CP holds in simple systems.

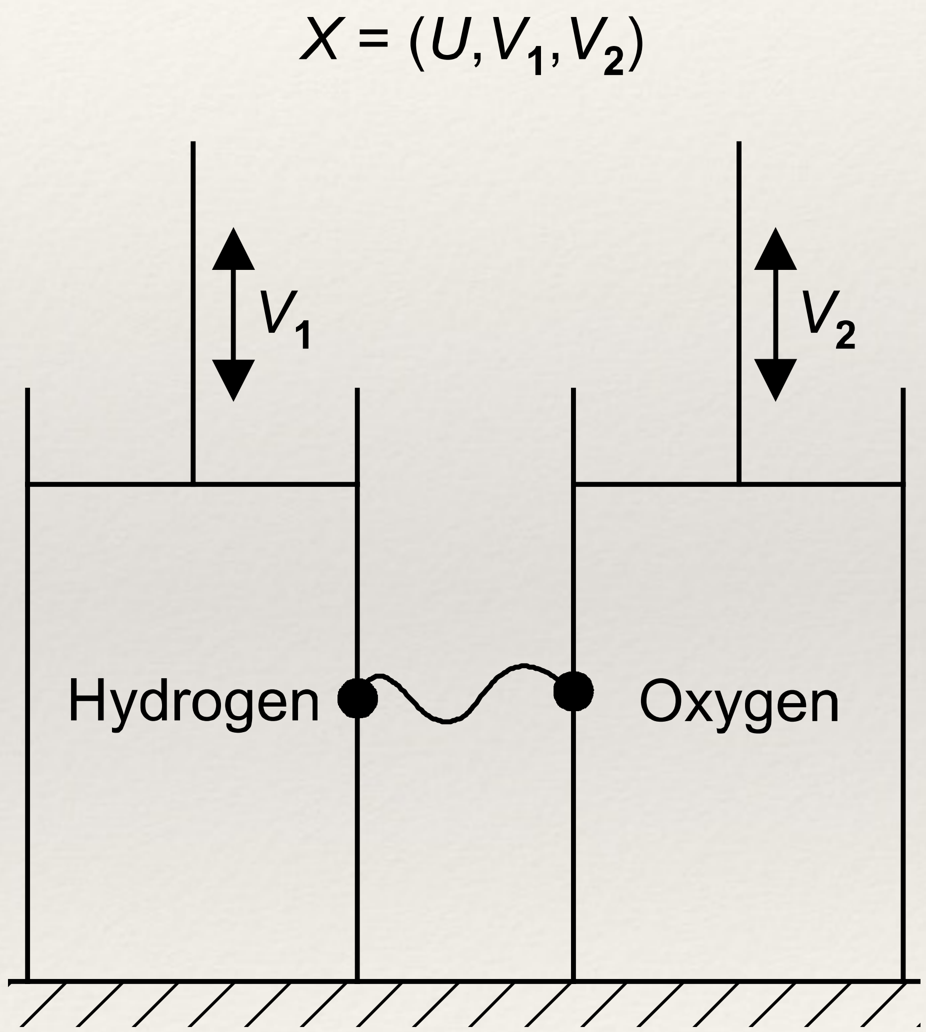
Axioms for Thermal Equilibrium

(T1) Thermal contact

- For any two simple systems, there is another simple system, the **thermal join**, with convex state space Δ_{12}.
- Moreover,

$$((U_1, V_1), (U_2, V_2)) \prec (U_1 + U_2, V_1, V_2)$$

$$X \in \Delta_{12}$$



(T2) Thermal splitting

For any point $(U, V_1, V_2) \in \Delta_{12}$ there is at least one pair of states, $(U_1, V_1) \in \Gamma_1$, $(U_2, V_2)) \in \Gamma_2$, with $U = U_1 + U_2$, such that

$$(U, V_1, V_2) \overset{A}{\sim} ((U_1, V_1), (U_2, V_2)).$$

In particular, if (U, V) is a state of a simple system Γ and $\lambda \in [0, 1]$ then

$$(U, (1-\lambda)V, \lambda V) \overset{A}{\sim} (((1-\lambda)U, (1-\lambda)V), (\lambda U, \lambda V)) \in \Gamma^{(1-\lambda)} \times \Gamma^{(\lambda)}.$$

(T3) Zeroth law of thermodynamics

- Definition : **thermal equilibrium**

  If $((U_1, V_1), (U_2, V_2)) \overset{A}{\sim} (U_1 + U_2, V_1, V_2)$ we say that the states $X = (U_1, V_1)$ and $Y = (U_2, V_2)$ are in **thermal equilibrium** and write
  $$X \overset{T}{\sim} Y.$$

- **(T3)** If $X \overset{T}{\sim} Y$ & $Y \overset{T}{\sim} Z$, then $X \overset{T}{\sim} Z$

- Thm 4.1 (**Scaling invariance of thermal equilibrium**)
  $$X \overset{T}{\sim} Y \text{ implies } \mu X \overset{T}{\sim} \lambda Y \text{ for any } \mu, \lambda > 0$$

Direction of forward sectors

- The forward sectors of all simple systems point the same way.

Proof Assum $(U_1+U_2,V_1,V_2)\overset{A}{\sim}((U_1,V_1),(U_2,V_2))$

If $(U_1,V_1)\prec(U_1+\delta,V_1)$ and $(U_2,V_2)\prec(U_2-\delta,V_2)$

$$(U,V_1,V_2)\prec(U+\delta,V_1,V_2) \text{ and } (U,V_1,V_2)\prec(U-\delta,V_1,V_2)$$

Contradiction to the Planck's principle ■

Maximum entropy principle

- If S is an entropy function of a simple system, then S is a concave function of U for fixed V. [note]
- If S_1 and S_2 are consistent entropy functions on two simple systems Γ_1 and Γ_2, then $(U_1, V_1) \overset{T}{\sim} (U_2, V_2)$ holds if and only if the sum of entropies takes its maximum value at $(U_1, V_1), (U_2, V_2)$ for fixed total energy and fixed work coordinates. That is, $(U = U_1 + U_2)$

$$\max_W [S_1(W, V_1) + S_2(U - W, V_2)] = S_1(U_1, V_1) + S_2(U_2, V_2)$$

(T4) Transversality

- If Γ is the state space of a simple system and if $X \in \Gamma$, then there exist states $X_0 \overset{T}{\sim} X_1$ with $X_0 \prec\prec X \prec\prec X_1$.
- Remark
  - **T4** implies **S1**.
  - Weaker condition $X_0 \prec X \prec X_1$ with $X_0 \prec\prec X_1$ is sufficient at this moment, but this does not imply **S1**. The strong version will be needed later, however.

(T5) Universal temperature range

If Γ_1 and Γ_2 are simple systems then, for every $X \in \Gamma_1$ and every $V \in \rho(\Gamma_2)$, where ρ is a projection on the work coordinates $\rho(U, V) := V$, there is $Y \in \Gamma_2$ with $\rho(Y) = V$ such that $X \overset{T}{\sim} Y$

- Remarks
  - The term temperature is used only for a mnemonic.
  - Physical motivation : Sufficient large copy of X is a **heat bath** and it is always possible for Y with fixed work coordinates to be in thermal equilibrium with the heat bath.

Comparison Principle in Compound Systems

Lemma 4.1 Extension of strips

- *For any state space (of a simple or compound system), if* $X_0 \prec\prec X_1$, $X_0' \prec\prec X_1'$ *and if*

$$X \overset{A}{\sim} ((1-\lambda)X_0, \lambda X_1),$$
$$X_1 \overset{A}{\sim} ((1-\lambda_1)X_0', \lambda_1 X_1'),$$
$$X_0' \overset{A}{\sim} ((1-\lambda_0)X_0, \lambda_0 X_1),$$

then

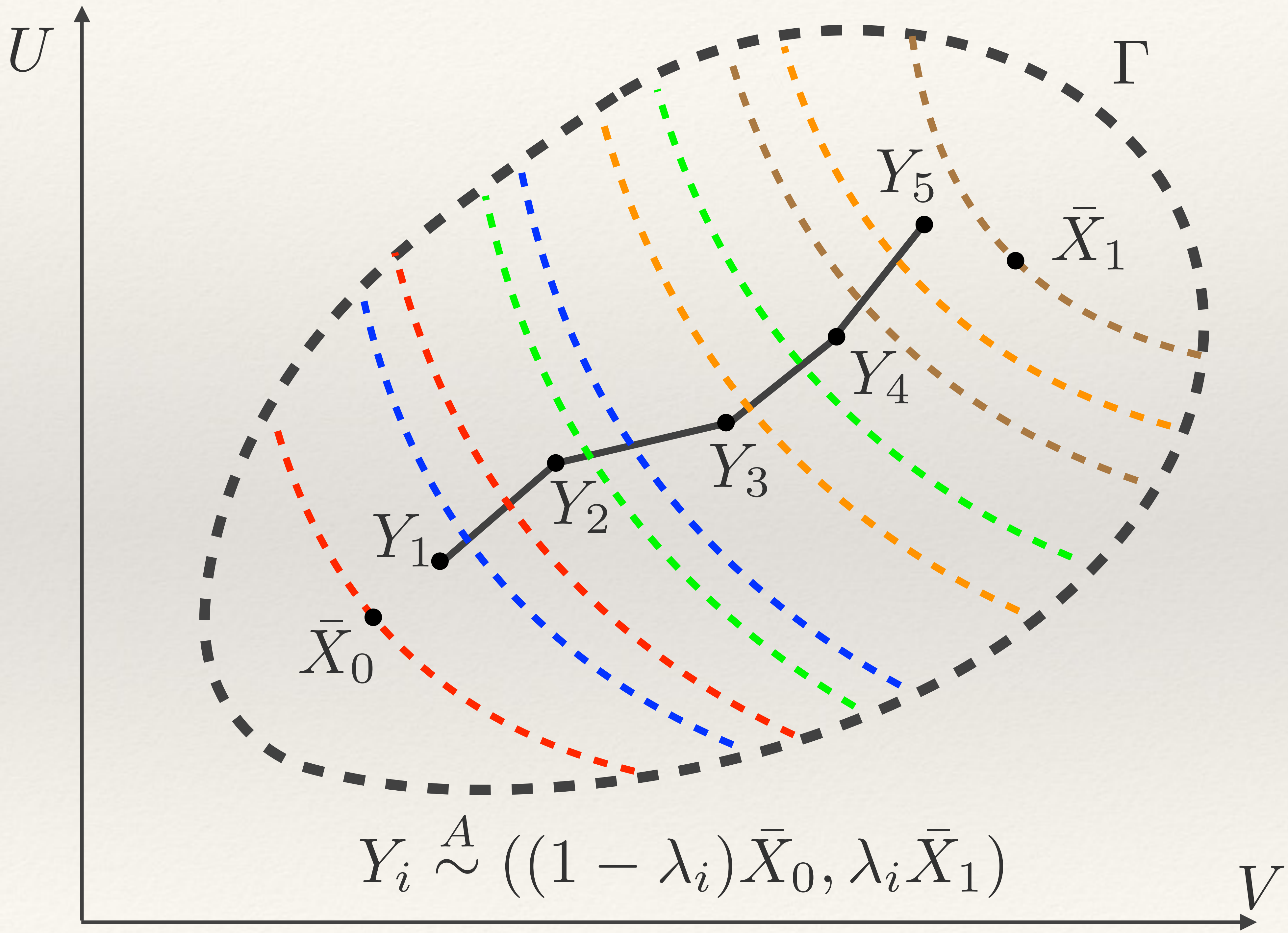
$$X \overset{A}{\sim} ((1-\mu)X_0, \mu X_1') \ \textit{with} \ \mu = \frac{\lambda\lambda_1}{1-\lambda_0+\lambda_0\lambda_1}$$

CP in multiple scaled copies

Let Γ *be a simple system and let* $a_1, \ldots, a_N, b_1, \ldots, b_M$ *be positive real numbers with* $a_1 + \cdots + a_N = b_1 + \cdots + b_M$. *Then all points in* $\Gamma^{(a_1)} \times \cdots \times \Gamma^{(a_N)}$ *are comparable to all points in* $\Gamma^{(b_1)} \times \cdots \times \Gamma^{(b_M)}$. *WLOG, we can set* $a_1 + \cdots + a_N = 1$.

- Once the above theorem is established, we can define, by Thm 2.2, unique entropy for this system up to affine transformation.
- We need especially **A5,T2,T4**, and Lemma 4.1.

Sketch of the proof



Criterion for comparison

Let Γ_1 *and* Γ_2 *be two (possibly unrelated) state spaces. Assume there is a relation* $\prec$ *satisfying axioms A1-A6 that holds for* Γ_1, Γ_2 *and their scaled products. Additionally,* $\prec$ *satisfies the* **CP** *on* Γ_1 *and its multiple scaled copies and on* Γ_2 *and its multiple scaled copies but, a priori, not necessarily on* $\Gamma_1 \times \Gamma_2$ *or any other products involving both* Γ_1 *and* Γ_2

If there are points $X_0, X_1 \in \Gamma_1$ *and* $Y_0, Y_1 \in \Gamma_2$ *such that*

$$X_0 \prec\prec X_1, \quad Y_0 \prec\prec Y_1$$

$$(X_0, Y_1) \overset{A}{\sim} (X_1, Y_0),$$

then the **CP** *holds on products of any number of scaled copies of* Γ_1 *and* Γ_2*.*

Entropy calibrator

- A quadruple of points satisfying

$$X_0 \prec\prec X_1, \quad Y_0 \prec\prec Y_1, \quad (X_0, Y_1) \overset{A}{\sim} (X_1, Y_0)$$

plays a role of ***entropy calibrator***.

- The existence of entropy calibrator is guaranteed by the thermal axioms T1~T4.
- To conclude, S1~S3 and T1~T5 guarantee the CP and the entropy principle is proved.

Temperature is epilogue rather than prologue.

Temperature

- Differentiability
- Isotherms and Adiabats
- Thermal Equilibrium

Differentiability of Entropy

Upper and lower temperatures

- Definition of upper and lower temperatures at state X

$$1/T_{\pm}(X) = \lim_{\varepsilon \to \pm 0} \frac{1}{\varepsilon} \left[S(U + \varepsilon, V) - S(U, V) \right]$$

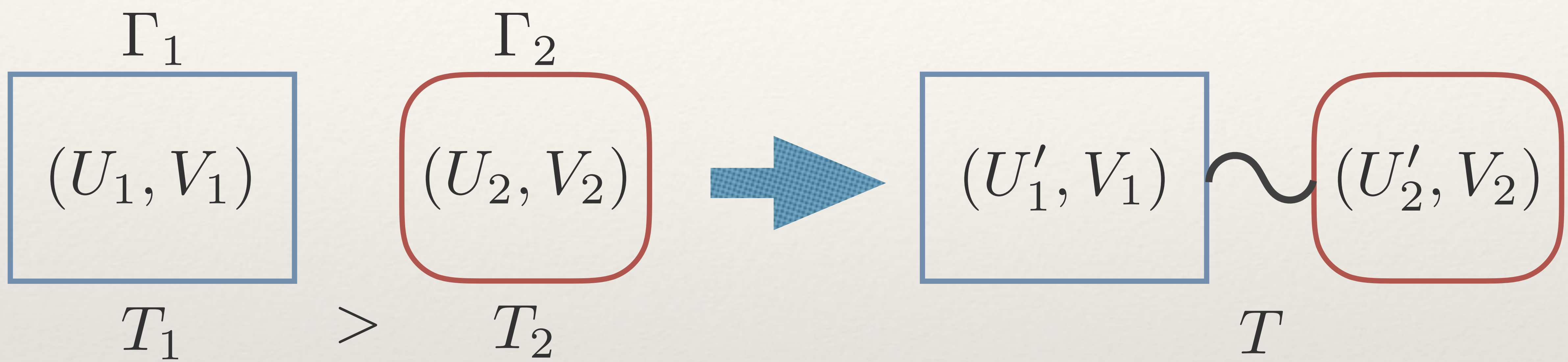
- Remark
  - Two temperatures are defined for any state. [note]
  - By Planck's principle, temperature is *positive*.
  - If $U_1 < U_2$, [note]

$$T_{-}(U_1, V) \le T_{+}(U_1, V) \le T_{-}(U_2, V) \le T_{+}(U_2, V)$$

Properties

- Continuity of the temperatures on adiabats.
- Uniqueness of temperature
- Continuity of temperature
- Differentiability of S

Energy flow (Clausius)

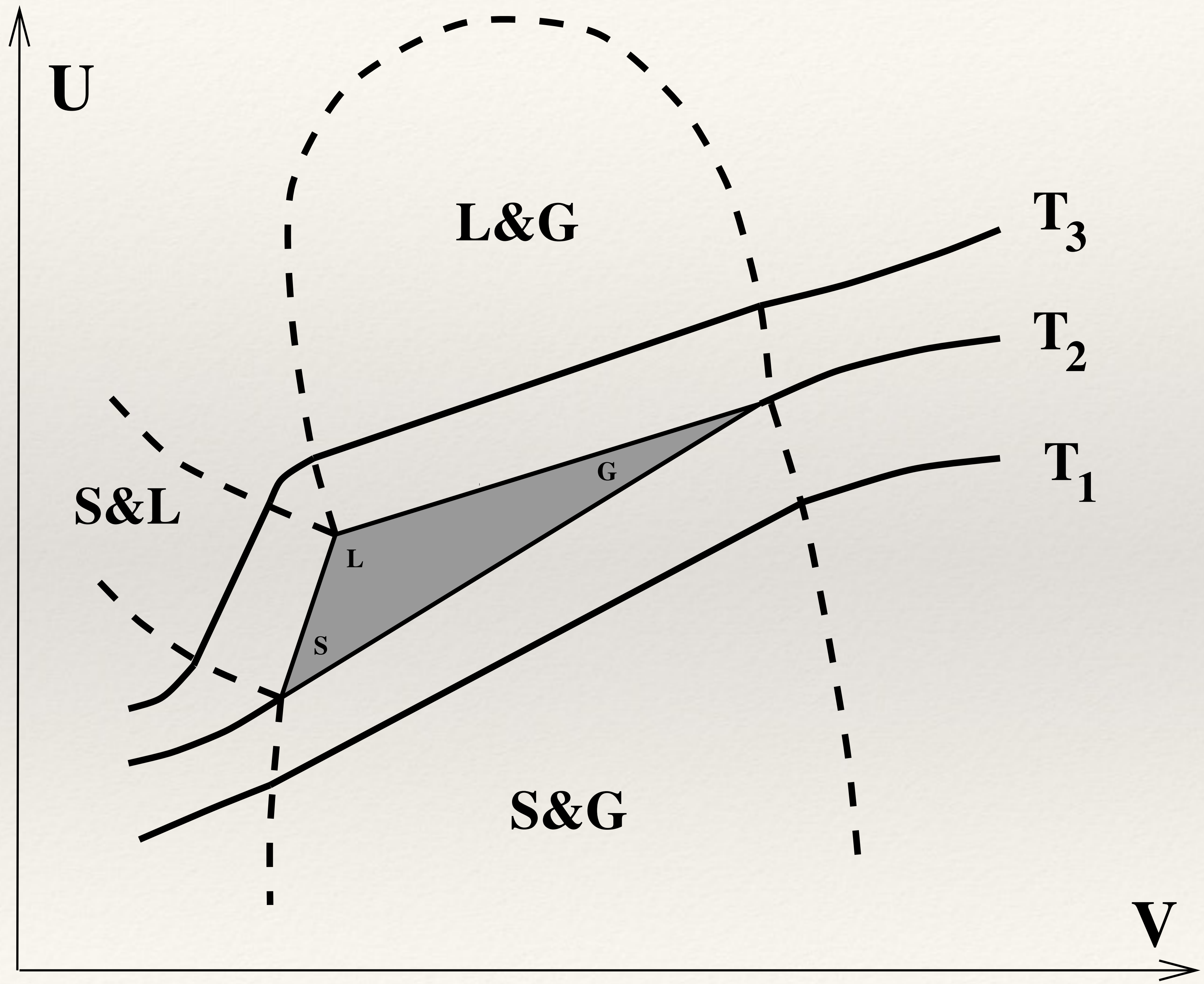


$$U_1 > U_1', \quad U_2 < U_2'$$

- Existence of T is guaranteed by **T1** and **T2**.
- U is an increasing function of T for fixed V.

Isotherms and Adiabats

Istotherms may have finite volume



Isotherms cut adiabats

Suppose $X_0 \prec X \prec X_1$ *with* $T(X_0) = T(X_1) = T_0$.

(1) *If* $T_{\min} < T_0 < T_{\max}$ *then there is a point* $X' \overset{A}{\sim} X$ *with* $T(X') = T_0$. *I.e., the isotherm cuts every adiabat.*

(2) *If* $T_0 = T_{\max}$, *either there is an* $X' \overset{A}{\sim} X$ *with* $T(X') = T_0$, *or, for any* $T_0' < T_0$ *there exist points* X_0', X' *and* X_1' *with* $X_0' \prec X' \overset{A}{\sim} X \prec X_1'$ *and* $T(X_0') = T(X') = T(X_1') = T_0'$.

(3) *If* $T_0 = T_{\min}$, *either there is an* $X' \overset{A}{\sim} X$ *with* $T(X') = T_0$, *or, for any* $T_0' > T_0$ *there exist points* X_0', X' *and* X_1' *with* $X_0' \prec X' \overset{A}{\sim} X \prec X_1'$ *and* $T(X_0') = T(X') = T(X_1') = T_0'$.

Adiabats and isotherms determine the entropy

Let $\prec$ and $\prec^*$ be two relations on the multiple scaled copies of a simple system Γ satisfying axioms A1–A7, S1–S3 and T1–T5. Let $\overset{T}{\sim}$ and $\overset{T}{\sim}{}^*$ denote the corresponding relations of thermal equilibrium between states in Γ. If $\prec$ and $\prec^*$ coincide on Γ and the same holds for the relations $\overset{T}{\sim}$ and $\overset{T}{\sim}{}^*$, then $\prec$ and $\prec^*$ coincide everywhere. In other words: The adiabats in Γ together with the isotherms determine the relation $\prec$ on all multiple scaled copies of Γ and hence the entropy is uniquely determined up to an affine transformation of scale.

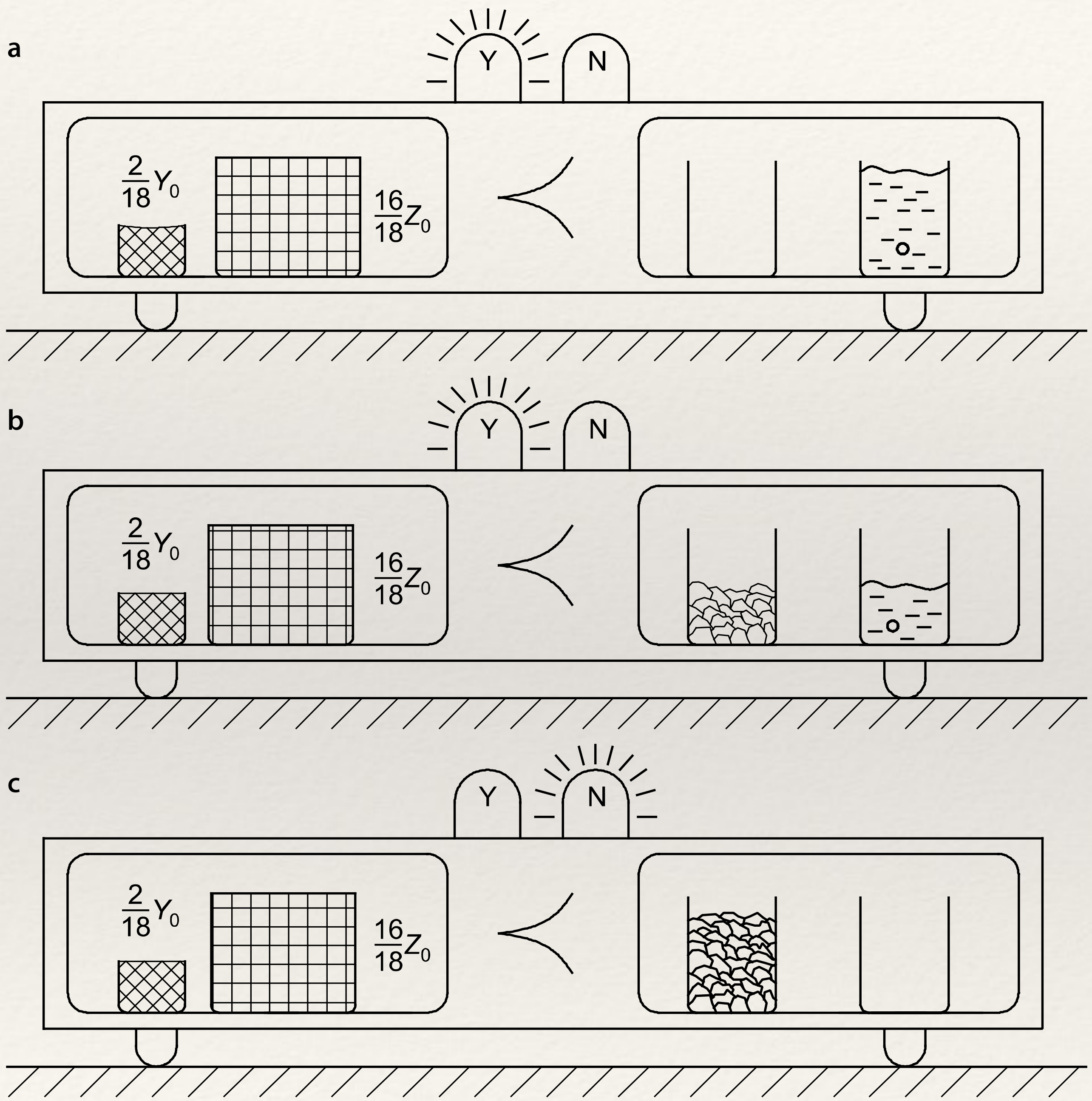
Mixing and Chemical Reactions

Entropy Constants

Entropy of mixture

- Entropy is defined for all systems *up to an additive constants*!
- But the additive constants are important for the entropy to dictate the order relation between two states in two different systems. (2 moles of hydrogen + 1 mole of Oxygen vs. 2 moles of water)
- Goal : to find additive constants which are additive and extensive and which dictates the order relation.

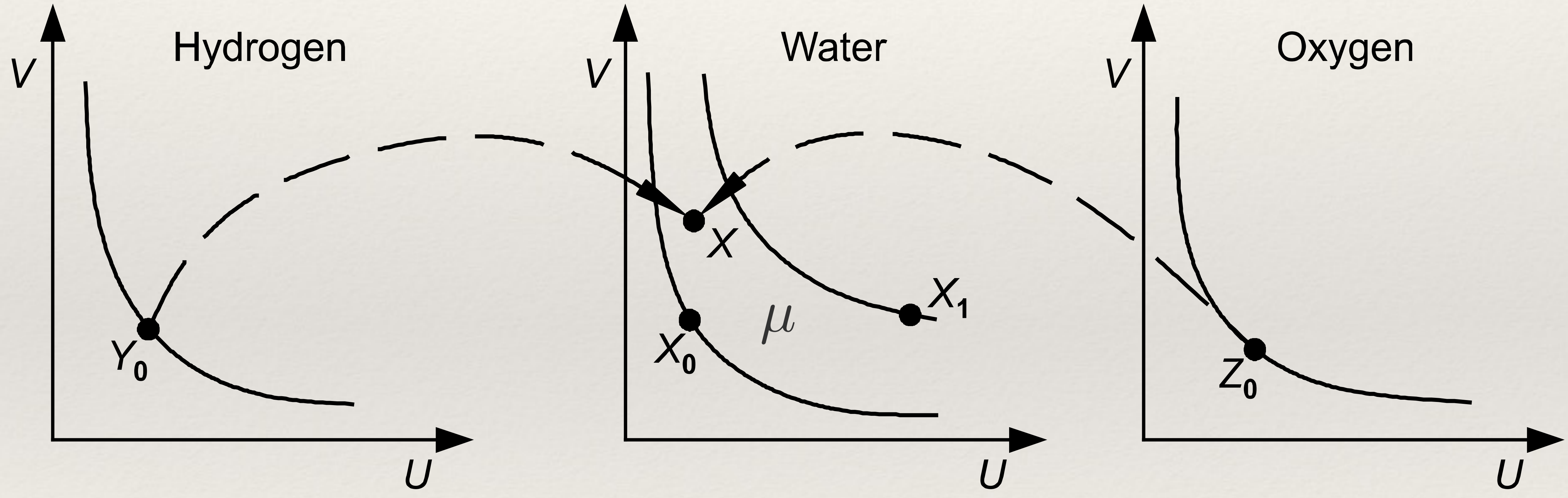
Heuristic Argument [T]



$$\frac{2}{18}S_0^{H_2} + \frac{16}{18}S_0^{O_2}$$
$$=(1-\mu)S_0^{H_2O} + \mu S_1^{H_2O}$$

Additive constants cannot be arbitrary!

Heuristic Argument [T]



Additive and Extensive Entropy

Our goal is to find constants $B(\Gamma)$, one for each state space Γ, in such a way that the entropy defined by

$$S(X) := S_\Gamma(X) + B(\Gamma) \quad \text{for} \quad X \in \Gamma$$

satisfies $S(X) \leq S(Y)$ whenever $X \prec Y$ with $X \in \Gamma$, $Y \in \Gamma'$. Since the initial entropies $S_\Gamma(X)$ already satisfy additivity and extensivity, additive constants $B(\Gamma)$ should satisfy

$$B(t_1\Gamma_1 \times t_2\Gamma_2) = t_1 B(\Gamma_1) + t_2 B(\Gamma_2)$$

for all state spaces Γ_1, Γ_2 under consideration and $t_1, t_2 > 0$.

Nonequilibrium Entropy

Axiomatic Approach

Master Equation

Axiomatic Approach [LY3]

Non-equilibrium states

- As before, we also consider equilibrium state spaces.
- Extended state space includes all non-equilibrium states as well as equilibrium states. $\Gamma \subset \hat{\Gamma}$
- One important requirement is the reproducibility, which is not at all obvious.
- In many cases, non-equilibrium states are either time-dependent or in contact with a heat bath with energy flux.

Assumptions

- Same order relation is defined in the extended space.
- A4 (scaling) and A5 (splitting) is not required.
- **Axiom N1**. **A1, A2, A3, A6** are satisfied.
- **Axiom N2**. For every $X \in \hat{\Gamma}$, there are $X', X'' \in \Gamma$ such that $X' \prec X \prec X''$.
- Non-equilibrium entropy preserving the order relation?

Entropy functions

For $X \in \hat{\Gamma}$ define

$$S_-(X) := \sup\{S(X') \ : \ X' \in \Gamma, X' \prec X\}$$

$$S_+(X) := \inf\ \{S(X'') \ : \ X'' \in \Gamma, X \prec X''\}$$

Properties of entropy functions

(a) $-\infty < S_\pm(X) < +\infty$ for all $X \in \hat{\Gamma}$.

(b) $S_\pm(X) = S(X)$ for $X \in \Gamma$, and $S_-(X) \leq S_+(X)$, for all $X \in \hat{\Gamma}$.

(c) The sup and inf in the definition of $S_\pm$ are attained for some $X', X'' \in \Gamma$ with $X' \prec X \prec X''$.

(d) $X \prec Y$ implies $S_-(X) \leq S_-(Y)$ and $S_+(X) \leq S_+(Y)$.

Properties of entropy functions

(e) If $S_+(X) \leq S_-(Y)$, then $X \prec Y$.

(f) Under composition, S_- is superadditive and S_+ subadditive, i.e.,

$$S_-(X_1) + S_-(X_2) \leq S_-(X_1, X_2)$$

$$S_+(X_1, X_2) \leq S_+(X_1) + S_+(X_2)$$

(g) If $\hat{S}$ is any function on $\hat{\Gamma}$ that coincides with S on Γ and is such that $X \prec Y$ implies $\hat{S}(X) \leq \hat{S}(Y)$, then $S_-(X) \leq \hat{S}(X) \leq S_+(X)$.

CP and uniqueness

The following are equivalent:

(i) *unique* $\hat{S}$ extending S such that $X \prec Y \Rightarrow \hat{S}(X) \leq \hat{S}(Y)$.

(ii) $S_-(X) = S_+(X)$ for all $X \in \hat{\Gamma}$.

(iii) There exists a (necessarily unique!) $\hat{S}$ extending S such that $\hat{S}(X) \leq \hat{S}(Y)$ implies $X \prec Y$.

(iv) The CP is valid on $\hat{\Gamma}$.

(v) Every $X \in \hat{\Gamma}$ is comparable with every $Z \in \Gamma$.

(vi) Every $X \in \hat{\Gamma}$ is adiabatically equivalent to some $Z \in \Gamma$.

Master Equation [van Kampen]

Master Equation and H function

- Master equation with a stationary state

$$\frac{dp_n}{dt} = \sum_{n'} \left(W_{nn'} p_{n'} - W_{n'n} p_n \right), \sum_{n'} \left(W_{nn'} p^e_{n'} - W_{n'n} p^e_n \right) = 0$$

- Let $f(x)$ be a nonnegative convex function.

$$0 \leq x < \infty, \quad f(x) \geq 0, \quad f''(x) > 0$$

- Define a quantity H by

$$H(t) := \sum_n p^e_n f\left(\frac{p_n(t)}{p^e_n}\right) = \sum_n p^e_n f(x_n) \geq 0$$

Time Evolution of H function

$$\frac{dH}{dt} = \sum_{nn'} f'(x_n)\left(W_{nn'}p_{n'} - W_{n'n}p_n\right)$$

$$= \sum_{nn'} W_{nn'}p^e_{n'}\left\{x_{n'}f'(x_n) - x_{n'}f'(x_{n'})\right\}$$

- Since $\sum_{nn'} W_{nn'}p^e_{n'}\left(\psi_n - \psi_{n'}\right)$ for any ψ_n,

  choosing $\psi_n = f(x_n) - x_n f'(x_n)$ gives

$$\frac{dH}{dt} = \sum_{nn'} W_{nn'}p^e_{n'}\left\{(x_{n'} - x_n)f'(x_n) + f(x_n) - f(x_{n'})\right\} \leq 0$$

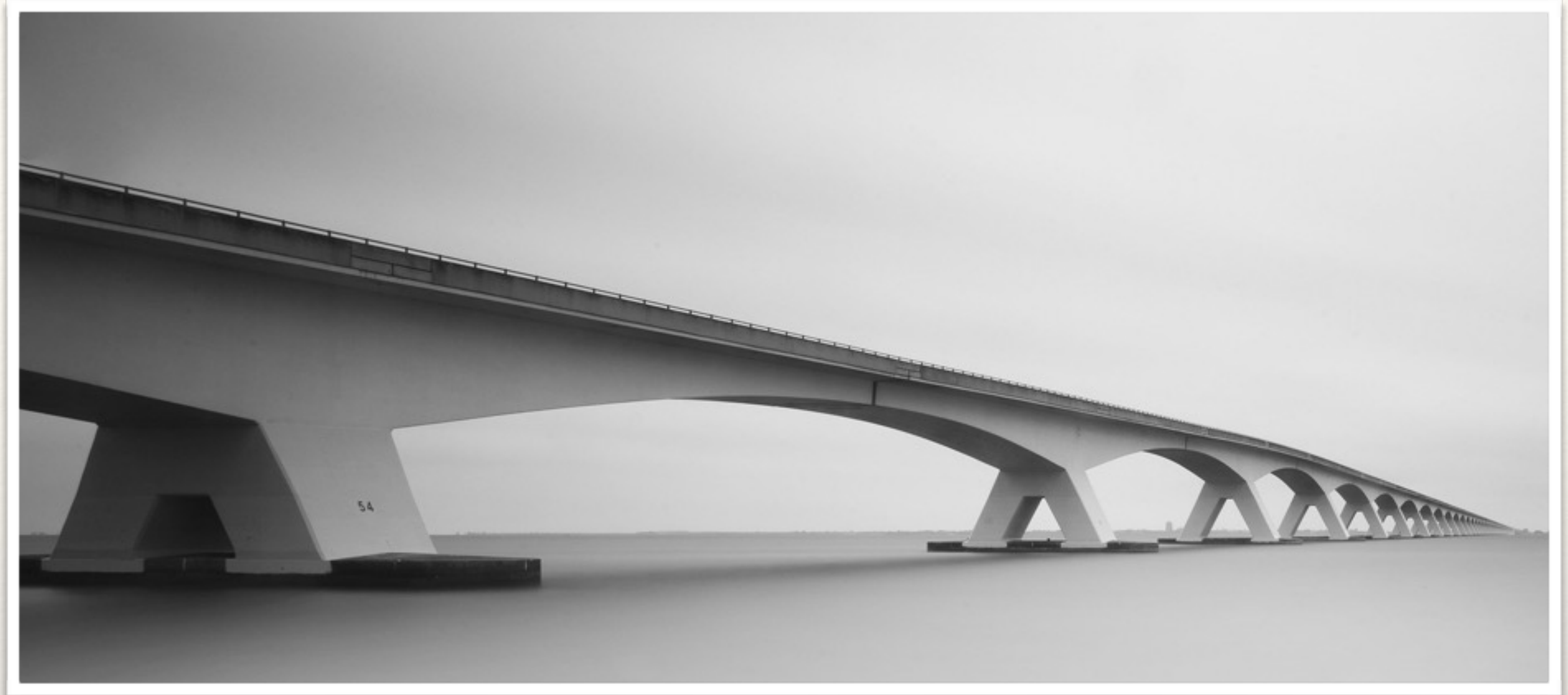
Time Evolution of H function

- H must have a well-defined limit (if n is finite).
- H is 0 if $x_n = x_{n'}$ **(steady state)** and $f(1) = 0$.
- One customarily chooses

$$f(x) = x \ln x, \quad H = \sum_n p_n \ln \frac{p_n}{p_n^e}$$

- H is extensive.
- Generalized (extensive) entropy

$$S = -kH + S^e$$



To be continued.

- Several axioms are equivalent to the existence of entropy with the behavior we expect.
- One way of proving the 2nd law from stat mech approach : To show that microscopic dynamics satisfy the axioms, at least for large systems.
- Themodynamics of small systems, like DNA? Can we define a sensible internal energy for small systems?
- Quantum mechanical definition of work? This is important because internal energy and, accordingly, thermodynamic quantities are only defined by works.