A Crash Course on Thermodynamics and Entropy

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“A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.”

A. Einstein (1946)

Thermodynamics is one of the three pillars of classical physics, the other two being mechanics and electrodynamics.

Thermodynamics is concerned with interactions (usually in the form of energy exchange) between macroscopic bodies where ”temperature” plays a role.

”Temperature” is not a simple concept, however. More fundamental is ENTROPY, from which temperature arises through differentiation with respect to the internal energy.

The central role of Entropy is to determine which changes of thermodynamical systems are possible under ”adiabatic conditions” and which are not: The SECOND LAW OF THERMODYNAMICS says that the entropy must never decrease under such conditions.

In the form of this ENTROPY PRINCIPLE the second law leads to the classical formulas for the maximal efficiency of heat engines, e.g., the Carnot efficiency

$$\eta \leq \left(1 - \frac{T_\ell}{T_h}\right)$$

It also leads to a formula for available energy (also called exergy) which is the maximal amount of work that can be obtained from a system in a given surrounding:

$$\Phi = (U - U_0) - T_0(S - S_0)$$

The entropy principle allows to answer questions like:

- What is the maximal electric power that can be extracted from a 2 km deep borehole delivering 100 l/sec of water at 350° C?
- How much available energy is contained in a million ton iceberg swimming in the Gulf Stream?

- What is the minimum kerosine consumption of a jet engine producing a thrust of 1000 kp?

- How much energy does an air conditioning need in order to change the state of 1 cubic meter of air at atmospheric pressure from 40° C and 90 % humidity to 20° C and 10 % humidity?

Entropy also leads to surprising relations between quantities that at first sight are unrelated since they are measured with very different means and do not involve entropy directly. Examples:

$$\frac{m\,v_{\mathrm{sound}}^2}{RT} = \frac{c_P}{c_V}, \qquad \frac{dP}{dT} = \frac{\Delta h}{T\Delta v}, \qquad \frac{d}{dT}\ln K(T) = \frac{(\Delta H)^2}{RT^2}$$

THE CLASSICAL FORMULATIONS

CLAUSIUS:

No process is possible the sole result of which is that heat is transferred from a body to a hotter one.

KELVIN-PLANCK:

No process is possible the sole result of which is that a body is cooled and a weight is raised.

CARATHÉODORY:

In the neighbourhood of any state there are states which cannot be reached from it by an adiabatic process.

Each of these statements is supposed to lead to the concept of entropy, but a mathematically rigorous derivation based on them is not simple.

Many hidden assumptions!

Are concepts like “heat”, “cooling” etc, or idealized Carnot engines really essential for the Second Law?

The Second Law in the form of the Entropy Principle is one of the few really fundamental physical laws. It is independent of models and its consequences are far reaching. Deserves a simple and solid logical foundation!

SUBJECT OF THE COURSE:

An approach to the basic principles behind the second law, in particular a **definition of entropy**, based solely on the concept of **adiabatic accessibility** without recourse to Carnot cycles, ideal gases or statistical mechanical models.

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BASIC EMPIRICAL FACT:

Under “adiabatic conditions”, certain changes of the equilibrium states of thermodynamical systems are possible and some are not.

SECOND LAW OF THERMODYNAMICS:

The possible state changes are characterized by the increase (non-decrease) of an (essentially) unique state function, called **ENTROPY**, that is extensive and additive on subsystems.

Paradigmatic situation:

System

+ Gorilla equipped with some machinery

+ a weight

The Second Law predicts what the gorilla can do and what it can't.

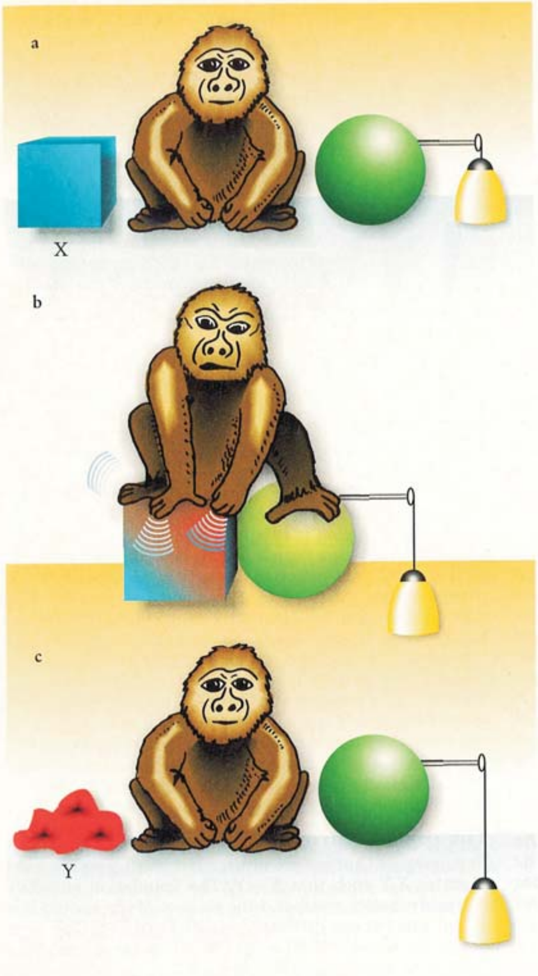


FIGURE 1. THE SECOND LAW OF THERMODYNAMICS says that increased entropy characterizes those final states of a macroscopic system that can be reached from a given initial state without leaving an imprint on the rest of the universe, apart from the displacement of a weight. The scenario shown here illustrates that the process can be quite violent. (**a**) A system in an equilibrium state X (blue) is placed in a room with a gorilla, some intricate machinery (green), and a weight. (**b**) The gorilla, machinery, and system interact and the system undergoes a violent transition. (**c**) The system is found in a new equilibrium state Y (red), the gorilla and machinery are found in their original state, while the weight may have been displaced. The role of the weight is to supply energy (via the machinery) both for the actions of the gorilla and for bringing the machinery and gorilla back to their initial states. The recovery process may involve additional interactions between machinery, system, and gorilla—interactions besides those indicated in (**b**).

BASIC CONCEPTS:

Thermodynamical systems, simple or compound

Equilibrium states $X, X' \dots$ and state spaces $\Gamma, \Gamma', \dots$

Composition of states, $(X, X') \in \Gamma \times \Gamma'$

Scaled copies, $\lambda X \in \lambda\Gamma$

BASIC RELATION BETWEEN STATES:

Adiabatic accessibility, denoted by

$$\prec$$

OPERATIONAL DEFINITION:

A state Y *is adiabatically accessible from a state* X*, in symbols* $X \prec Y$*, if it is possible to change the state from* X *to* Y *in such a way that the only net effect on the surroundings is that a weight may have risen or fallen*

NOTATIONS:

If $X \prec Y$ *or* $Y \prec X$ we say that X and Y are *comparable*.

If $X \prec Y$ *but* $Y \not\prec X$ we say that X strictly precedes Y and write

$$X \prec\prec Y.$$

If $X \prec Y$ and $Y \prec X$ we say that X and Y are adiabatically equivalent and write

$$X \overset{\text{A}}{\sim} Y.$$

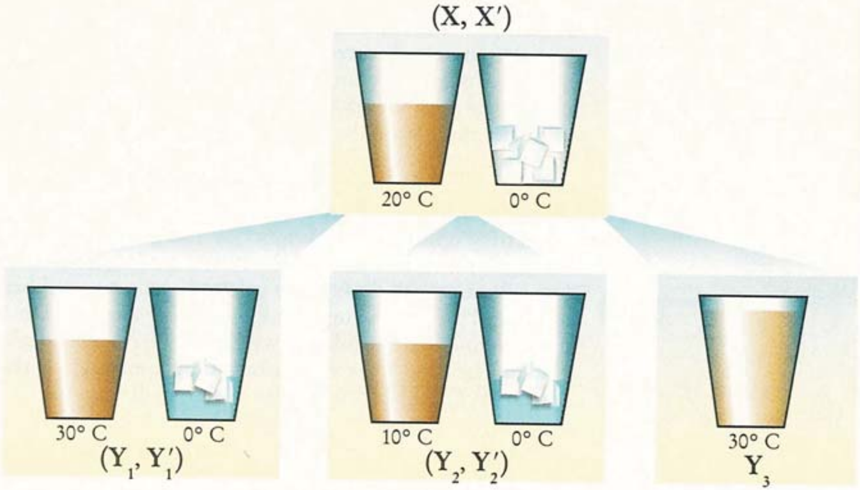


FIGURE 2. ADIABATIC STATE CHANGES for a compound system consisting of a glass of whiskey and a glass of ice. The states (Y_1,Y_1'), (Y_2,Y_2'), and Y_3 are all adiabatically accessible from (X,X'). (Y_1,Y_1') can be reached by weight-powered stirrers (not shown) acting on each glass. (Y_2,Y_2') is obtained by bringing the two subsystems temporarily into thermal contact. Y_3 is obtained by pouring the whiskey on the ice and stirring; this is a mixing process and changes the system. The original state (X,X') is *not* adiabatically accessible from any of the three states (Y_1,Y_1'), (Y_2,Y_2'), or Y_3.

SECOND LAW (ENTROPY PRINCIPLE):

There is a function called **entropy**, defined on all states and denoted by S, such that

a) **Monotonicity:** If X and Y are comparable, then

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

b) **Additivity and extensivity:** For compositions and scaled copies of states we have

$$S(X, X') = S(X) + S(X') \quad \text{and} \quad S(\lambda X) = \lambda S(X).$$

The codification of the list of state pairs that are adiabatically accessible from each other in terms of a single function S has enormous predictive power. The additivity and extensivity are also essential. First, they guarantee (essential) uniqueness and secondly they simplify greatly the experimental or theoretical determination of entropy. For instance, in order to predict the efficiency of a geothermal power plant it suffices to know the properties of 1 kg of $\mathrm{H_2O}$.

MAIN QUESTIONS:

Q1: Which properties of the relation $\prec$ ensure existence and (essential) uniqueness of entropy?

Q2: Can these properties be derived from simple physical premises?

FURTHER QUESTIONS:

Q3: Which convexity and smoothness properties of S follow from the premises?

Q4: Can temperature be defined from entropy and what are its properties?

Q5: Can the entropy of mixing or of a chemical reaction be determined without invoking ‘semipermeable membranes’?

THE CONDITIONS ON $\prec$:

A1. *Reflexivity*: $X \overset{\text{A}}{\sim} X$.

A2. *Transitivity:* If $X \prec Y$ and $Y \prec Z$, then $X \prec Z$.

A3. *Consistency*: If $X \prec X'$ and $Y \prec Y'$, then $(X, Y) \prec (X', Y')$

A4. *Scaling Invariance*: If $\lambda > 0$ and $X, Y \in \Gamma$ with $X \prec Y$, then $\lambda X \prec \lambda Y$

A5. *Splitting and Recombination*: $X \overset{\text{A}}{\sim} ((1-\lambda)X, \lambda X)$.

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

CP. *Comparison Property for Γ*: Any two states in $(1-\lambda)\Gamma \times \lambda\Gamma$ are comparable, for all $0 \leq \lambda \leq 1$.

Conditions (A1)-(A6) are all highly plausible if $\prec$ is interpreted as the relation of adiabatic accessibility in the sense of the operational definition.

Condition (CP) is not so simple, but it is essential for the existence of an entropy that characterizes the relation on compound systems made of scaled copies of Γ.

The conditions A1-A5, together with the cancellation law

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

(which follows either from the operational definition, or from A6, stability) implies that one can "compute" with the scalings and compositions exactly as with (positive and negative) real numbers with scaling corresponding to multiplication and the composition $(\cdot, \cdot)$ to addition. An important consequence is the following Lemma.

LEMMA 1: *If* $X_0 \prec\prec X_1$ *and* $\lambda, \lambda' \in [0,1]$, *then*

$$((1-\lambda)X_0, \lambda X_1) \prec ((1-\lambda')X_0, \lambda' X_1) \Leftrightarrow \lambda \le \lambda'.$$

Proof: Using the "arithmetics" for scaling and composition the left-hand side is equivalent to

$$(\lambda - \lambda')X_1 \prec (\lambda - \lambda')X_0,$$

which, if $(\lambda - \lambda') > 0$, would mean that $X_1 \prec X_0$, in contradiction to the assumption $X_0 \prec\prec X_1$. □

UNIQUENESS OF ENTROPY:

Pick two reference points $X_0 \prec\prec X_1$ in Γ and let X be an arbitrary state with $X_0 \prec X \prec X_1$. For any entropy function S we have $S(X_0) < S(X_1)$ and $S(X_0) \leq S(X) \leq S(X_1)$, so there is a unique λ between 0 and 1 such that

$$S(X) = (1 - \lambda)S(X_0) + \lambda S(X_1).$$

By the assumed properties of entropy this is equivalent to

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

Another entropy function S' also leads to the same equality with λ replaced by λ'. Lemma 1 now implies that this can hold for *at most* one λ.

Thus the entropy, provided it can be shown to exist, is unique up to the two arbitrary constants $S(X_0)$ and $S(X_1)$. A change of these constants amounts to an affine transformation, $S \to aS + b$.

PROOF OF EXISTENCE:

We claim that

$$\begin{aligned} \lambda^* &:= \sup\{\lambda : ((1-\lambda)X_0, \lambda X_1) \prec X\} \\ &\overset{!}{=} \inf\,\{\lambda : X \prec ((1-\lambda)X_0, \lambda X_1)\} \end{aligned}$$

does satisfy

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

Indeed, for the stability assumption A6 it follows that the sup is attained at some λ^- and the inf at some λ^+. Moreover, using transitivity, A2, one has

$$((1-\lambda^-)X_0, \lambda^- X_1) \prec ((1-\lambda^+)X_0, \lambda^+ X_1).$$

By Lemma 1 this is equivalent to

$$\lambda^- \leq \lambda^+.$$

If $\lambda^- < \lambda^+$ there would be a λ with $\lambda^- < \lambda < \lambda^+$ and hence, by Lemma 1,

$$((1-\lambda^-)X_0, \lambda^- X_1) \prec ((1-\lambda)X_0, \lambda X_1) \prec ((1-\lambda^+)X_0, \lambda^+ X_1).$$

Now, $((1-\lambda)X_0, \lambda X_1) \prec X$ would contradict the fact that λ^- is a sup, so by the comparability of all states in $(1-\lambda)\Gamma \times \lambda\Gamma$ we must have $X \prec ((1-\lambda)X_0, \lambda X_1)$. Here we have used A5, that allows to consider X as a state in $(1-\lambda)\Gamma \times \lambda\Gamma$.

In the same way one sees that $((1-\lambda)X_0, \lambda X_1) \prec X$. The claim now follows from A2 and Lemma 1.

Additivity and extensivity are easy consequences of A2-A5. $\square$

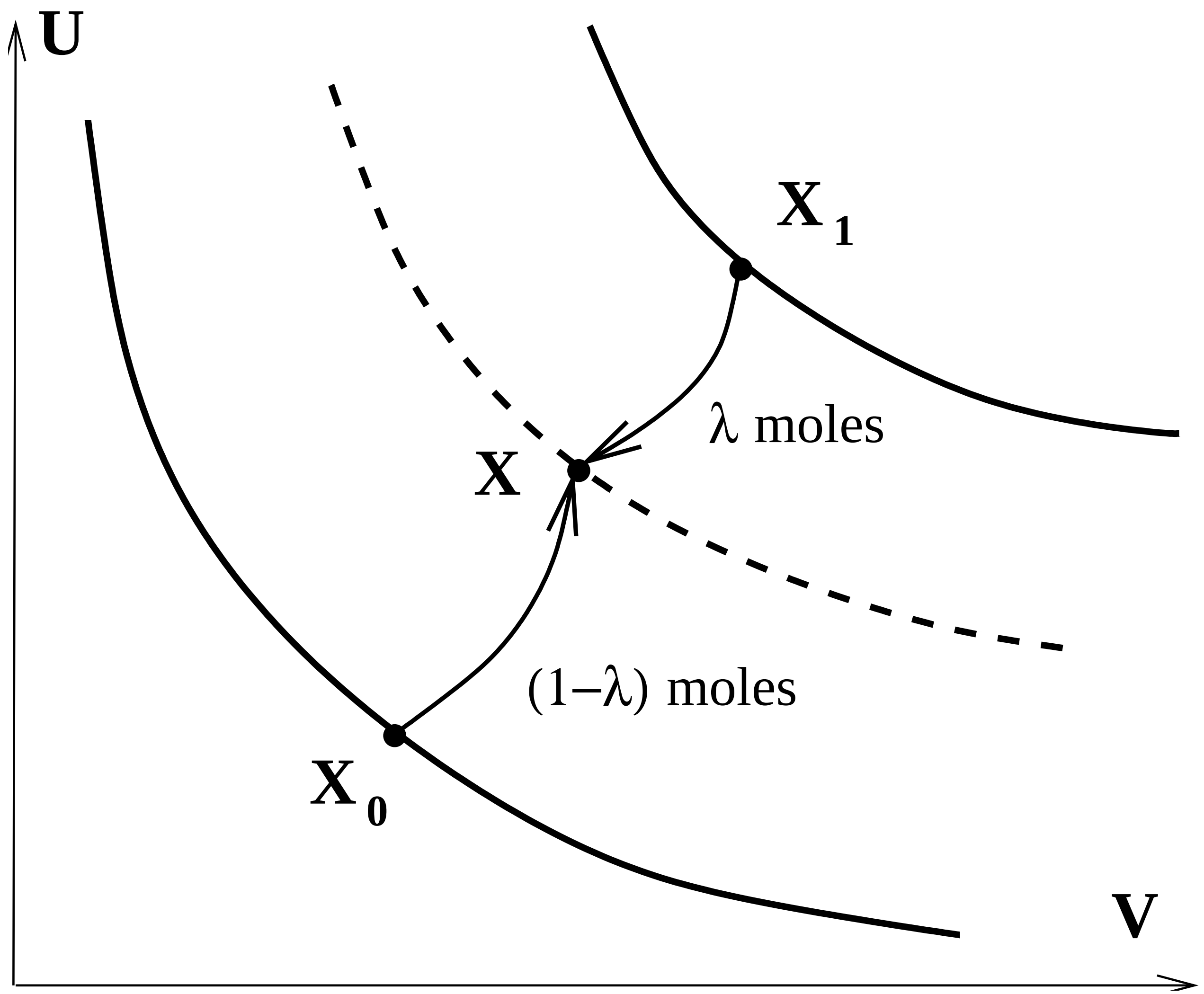
With the choice

$$S(X_0) = 0 \quad \text{and} \quad S(X_1) = 1$$

for some reference points $X_0 \prec\prec X_1$, we now have an **explicit formula for the entropy**

$$\begin{aligned} S(X) &= \sup\{\lambda : ((1-\lambda)X_0, \lambda X_1) \prec X\} \\ &= \inf\{\lambda : X \prec ((1-\lambda)X_0, \lambda X_1)\} \end{aligned}$$

that uses only the relation $\prec$ and makes neither appeal to Carnot cycles nor to statistical mechanics.


U
X₁
λ moles
X
(1–λ) moles
X₀
V

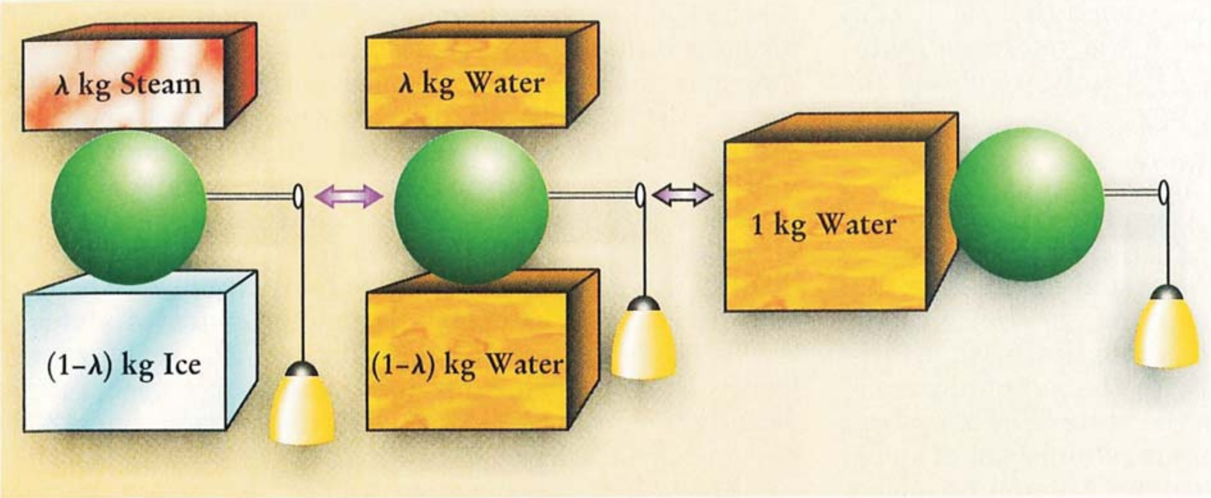


FIGURE 3. DEFINITION OF ENTROPY. One can define the entropy of 1 kg of water in a given state (represented by the orange color) by obtaining the state from a fraction λ kg of steam in a fixed, standard state (red) and a fraction $1 - \lambda$ kg of ice in a fixed, standard state (blue), with the aid of a device (green) and a weight (yellow). The device returns to its initial state at the end of the process, but the weight may end up raised or lowered. The entropy S_{water}, measured in units of S_{steam}, is the maximum fraction $\lambda = \lambda_{\text{max}}$ for which the transformation to 1 kg of water in the given (orange) state is possible. The system of steam and ice is used here only for illustration. The definition of entropy need not involve phase changes.

Using A2-A5 one can extend the previous considerations to arbitrary multiple scaled products of Γ:

THEOREM 1. (Entropy $\Longleftrightarrow$ A1-A6 & GP)

The following are **equivalent***:*

(1) The relation $\prec$ satisfies assumptions A1-A6 and the comparison property, CP, holds.

(2) There is a function S on Γ, such that if $X_1, \dots X_n, Y_1, \dots, Y_m \in \Gamma$ and $\sum_i \lambda_i = \sum_j \mu_j$, then

$$(\lambda_1 X_1, \dots, \lambda_n X_n) \prec (\mu Y_1, \dots, \mu_m Y_m)$$

if and only if

$$\lambda_1 S(X_1) + \dots + \lambda_n S(X_n) \leq \mu_1 S(Y_1) + \dots + \mu_n S(Y_n).$$

The function S is uniquely determined up to an affine transformation of scale.

A further generalization is the following

THEOREM 2. (Consistent entropy scales) *Assume that CP holds for all compound systems. For each system Γ let S_Γ be an entropy function on Γ in the sense of Theorem 1. Then there are constants a_Γ and b_Γ, such that the function S, defined for all states of all systems by*

$$S(X) = a_\Gamma S_\Gamma(X) + b_\Gamma$$

if $X \in \Gamma$, *is extensive and additive on all scaled compounds of all systems and characterizes* $\prec$ *in the sense that if* X *and* Y *are in the same state space, then*

$$X \prec Y \iff S(X) \leq S(Y).$$

Sketch of proof: One argues first that it is possible to pick for every Γ a reference point $X_\Gamma \in \Gamma$ in such that

$$X_{\Gamma_1 \times \Gamma_2} = (X_{\Gamma_1}, X_{\Gamma_2}) \quad \text{and} \quad X_{\lambda\Gamma} = \lambda X_\Gamma.$$

Then one chooses some fixed space Γ_0 and some points $Z_0 \prec\prec Z_1$ in Γ_0 and defines

$$\begin{aligned} S(X) &:= \sup\{\lambda : (X_\Gamma, \lambda Z_1) \prec (X, \lambda Z_0)\} \\ &\overset{!}{=} \inf\,\{\lambda : (X, \lambda Z_0) \prec (X_\Gamma, \lambda Z_1)\} \end{aligned}$$

This is readily seen to be an additive and extensive entropy function, and by the uniqueness it is related to S_Γ by an affine transformation. $\square$

To summarize, the main conclusion so far is:

The existence and (essential) uniqueness of entropy is **equivalent** to the (very natural) assumptions A1-A6 about the relation of adiabatic accessibility plus the comparison property, CP.

However, CP is not at all self evident, as can be seen by considering systems where “rubbing” and “thermal equilibration” are the only adiabatical operations.

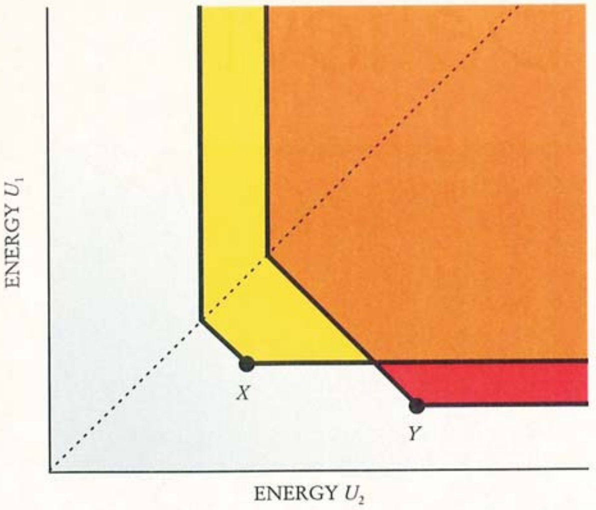


FIGURE 4. HYPOTHETICALLY NONCOMPARABLE STATES. The graph shows the state space of a pair of identical, incompressible solids with the energies U_1 and U_2 as the only coordinates of the compound system. The states adiabatically accessible from X (yellow/orange) and Y (red/orange) are shown under the assumption that the only adiabatic changes consist in combinations of rubbing (increasing U_1 or U_2) and thermal equilibration (moving to the diagonal $U_1 = U_2$). In this example, adiabatic accessibility *cannot* be characterized by an entropy function, because neither a transformation from X to Y nor from Y to X is possible. The comparison hypothesis does not hold here. In the real world, however, it *always* holds.

An essential part of our analysis is a derivation of CP from additional assumptions about SIMPLE SYSTEMS which are the basic building blocks of thermodynamics. At the same time we make contact with the traditional concepts of thermodynamic like pressure and temperature.