The entropy concept for non-equilibrium states

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Proc. Roy. Soc. A 469: 2013.0408

IMS Singapore, Sept. 12, 2013

Basic empirical fact:

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(Note: For *macroscopic systems* the distinction between the possible and the impossible is unambiguous. For meso- or microscopic systems probability may be involved and the distinction not as sharp, but that is not our concern here.)

Second Law of Thermodynamics:

For equilibrium states, at least, 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.

Remarks

The uniqueness is very important! It means that all methods to define entropy for equilibrium states lead to the same result, provided the basic requirements (that the entropy characterizes adiabatic accessibility and is additive and extensive) are fulfilled.

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The additivity and extensivity are also essential. First, they guarantee the (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 H_2O.

The mere existence of entropy satisfying the fundamental relation

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum_i \frac{\mu_i}{T}dn_i$$

leads to surprising connections between quantities that at first sight are unrelated, for instance:

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

Another consequence of the existence of entropy is a formula, due to Max Planck, that relates an arbitrary empirical temperature scale Θ to the absolute temperature scale T:

$$T(\Theta) = T_0 \exp \left(\int_{\Theta_0}^{\Theta} \frac{\left(\frac{\partial P}{\partial \Theta'}\right)_V}{P + \left(\frac{\partial U}{\partial V}\right)_{\Theta'}} \, d\Theta' \right)$$

The entropy determines also the maximal work that can be obtained from a system in an environment with temperature T_0:

$$\Phi_{X_0}(X) = (U - U_0) - T_0(S - S_0)$$

where X is the initial state with energy U and entropy S, and X_0 is the final state with energy U_0 and entropy S_0. (This quantity is also called availability or exergy.)

A quote:

"Boltzmann was right about atoms but utterly wrong in believing that atoms provided a necessary basis for thermodynamics. The second law does not require atoms. Thermodynamics would be equally correct if the basic constituents of the world were atoms, or quantum fields, or even strings."

L. Kadanoff

Mathematical facts:

- There is a very simple and direct approach to the existence and uniqueness of entropy of thermodynamical equilibrium states based only on properties of the relation of adiabatic accessibility. In particular, neither "heat", "temperature", "thermal reservoirs", nor statistical mechanics are needed for the definition of entropy.

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- The required properties are necessary for the existence of entropy and all very plausible except one: The adiabatic comparability of states.

More mathematical facts:

- For equilibrium states comparability can be derived from some further physical assumptions, but this requires substantially more work mathematically.

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- For non-equilibrium states an entropy characterizing the relation exists if and only if comparability holds and this in turn holds if and only if every state is adiabatically equivalent to an equilibrium state.

- This condition can not be expected to be fulfilled in general, in which case at least two entropy functions are needed.

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Basic relation between states:

Adiabatic accessibility, denoted by

$$X \prec Y$$

A state Y is **adiabatically accessible** from a state X, written $X \prec Y$ ('X precedes 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.

Important point: The process taking X to Y need not be "quasi-static" (let alone reversible). It can be arbitrarily violent!

Another important point: For the mathematical reasoning the physical interpretation of $\prec$ is irrelevant! The mathematics can be applied whenever the basic premises hold.

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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 $X \prec Y$.

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Notation: Two states, X and Y, are (adiabatically) comparable if either $X \prec Y$ or $Y \prec X$ holds. They are adiabatically equivalent, written $X \overset{A}{\sim} Y$ if both conditions hold. If $X \prec Y$ but $Y \not\prec X$ we write $X \prec\prec Y$.

The Comparison Property

Conditions (A1)-(A6) are all highly plausible if $\prec$ is interpreted as the relation of adiabatic accessibility in the sense of the operational definition. They are also clearly necessary, but still not sufficient for the existence of an entropy that characterizes the relation on compound systems made of scaled copies of Γ. A further property is needed:

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CP. *Comparison Property for scaled products of a state space Γ*:

Any two states in $(1 - \lambda)\Gamma \times \lambda\Gamma$ are comparable, for all $0 \leq \lambda \leq 1$.

Existence and uniqueness of equilibrium entropy

Theorem

*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 $X_1, \ldots X_n, Y_1, \ldots, Y_m \in \Gamma$ and $\sum_i \lambda_i = \sum_j \mu_j$, then*

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

if and only if

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

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

Proof of uniqueness

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 number λ between 0 and 1 such that

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

By the required properties of entropy this is equivalent to

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

Any other entropy function S' also leads to (*) with λ replaced by some λ', but from the assumptions A1-A6 and $X_0 \prec\prec X_1$ it follows easily that (*) can hold for at most one λ, i.e., $\lambda = \lambda'$.

From assumtions A1-A6 and CP it follows that

$$\lambda^* := \sup\{\lambda : ((1-\lambda)X_0, \lambda X_1) \prec X\}$$
$$\stackrel{!}{=} \inf\{\lambda : X \prec ((1-\lambda)X_0, \lambda X_1)\}$$

does satisfy

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

Note: Comparability of all states in $(1-\lambda)\Gamma \times \lambda\Gamma$ (not only of those in Γ) is essential!

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)\}
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Any other choice of $S(X_0)$ and $S(X_1)$ leads simply to an affine transformation of the values of S.

The special role of CP

We do not want to adopt CP as an axiom (although most authors do, usually without saying!) because we do not find it physically compelling. Our preference is to derive it from some more immediate assumptions. Consequently, an essential part our analysis and, in fact, mathematically the most complex one, is a derivation of CP from additional assumptions about simple systems which are the basic building blocks of thermodynamics. At the same time one makes contact with the traditional concepts of thermodynamics such as pressure and temperature.

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The additional assumptions concern a) the possibility to form combinations of states, b) existence of at east one irreversible state change from any give state and c) a continuity assumption about the pressure.

The bottom line is that CP is well established for equilibrium states!

Generalizations 1: Non-extensive entropies

The scaling assumption is not always natural (systems with long range forces, or when surface effects are important). The entropy for such a system Γ can be defined, however, by using a 'normal' system Γ_0 as an 'entropy meter' and defining for $X \in \Gamma$

$$
\begin{aligned}
S(X) &:= \sup\{S(Z) \,:\, (X_1, Z) \prec (X, Z_0)\} \\
&\overset{!}{=} \inf\{S(Z) \,:\, (X, Z_0) \prec (X_1, Z))\}.
\end{aligned}
$$

where $Z_0 \in \Gamma_0$ and $X_1 \in \Gamma$ are (arbitrarily chosen) reference points.

But, again, comparability of states is essential for the equality of sup and inf!

Generalizations 2: Non-equilibrium states

General remarks:

- There exist many variants of non-equilibrium thermodynamics: Classical Irreversible Thermodynamics, Extended Irreversible Thermodynamics, ...

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We assume that a relation $\prec$ is defined on $\hat{\Gamma}$ such that its restriction to Γ is characterized by an entropy function S as discussed previously.

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Basic question:

What are the possible extensions of S to $\hat{\Gamma}$ that are monotone w.r.t. $\prec$?

N1 The relation $\prec$ on $\hat{\Gamma}$ satisfies the assumptions A1 (Reflexivity), A2 (Transitivity), A3 (Consistency) and A6 (Stability) (but A4 (Scaling) and A5 (Splitting) are only required on Γ).

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N2 For every $X \in \hat{\Gamma}$ there are $X', X'' \in \Gamma$ such that $X' \prec X \prec X''$.

Non-equilibrium entropies

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

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\begin{aligned}
S_-(X) &:= \sup\{S(X') : X' \in \Gamma, X' \prec X\} \\
S_+(X) &:= \inf\{S(X'') : X'' \in \Gamma, X \prec X''\}
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Properties:

- Both functions are monotone with respect to $\prec$.

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Properties:

- Both functions are monotone with respect to $\prec$.
- Any other function on $\hat{\Gamma}$ that has this property lies between S_- and S_+.
- $(U - U_0) - T_0(S_+ - S_0) \leq \Phi_{X_0}(X) \leq (U - U_0) - T_0(S_- - S_0)$.

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(iv) Every $X \in \hat{\Gamma}$ is comparable with every $Y \in \hat{\Gamma}$, i.e., the Comparison Property holds on $\hat{\Gamma}$.

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(iv) Every $X \in \hat{\Gamma}$ is comparable with every $Y \in \hat{\Gamma}$, i.e., the Comparison Property holds on $\hat{\Gamma}$.

(v) Every $X \in \hat{\Gamma}$ is adiabatically equivalent to some $Z \in \Gamma$.
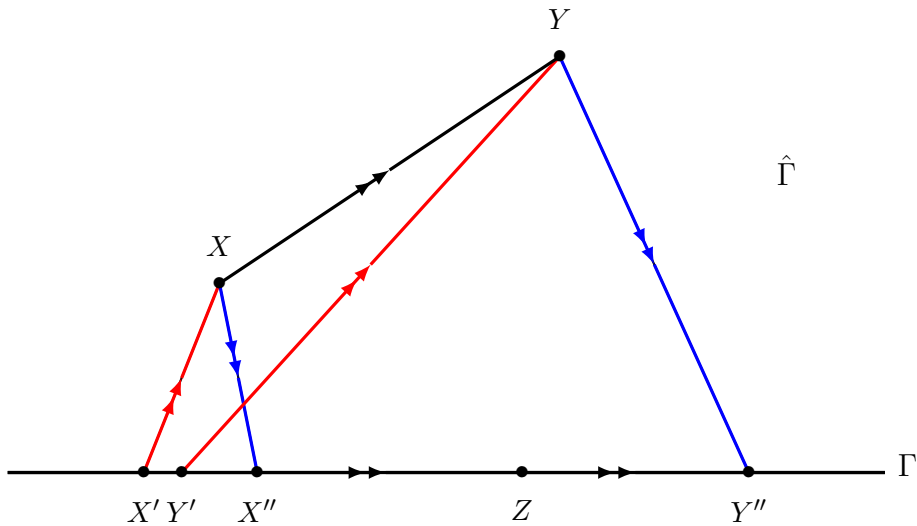
A toy example

The system consists of two identical pieces of copper glued together by a thin layer of finite heat conductivity. The state of the system as uniquely specified by the temperatures T_1 and T_2 of the two copper pieces. Mathematically, the state space $\hat{\Gamma}$ of this system is thus $\mathbb{R}_+^2$ with coordinates (T_1, T_2) and the equilibrium state space Γ is the diagonal, $T_1 = T_2$.
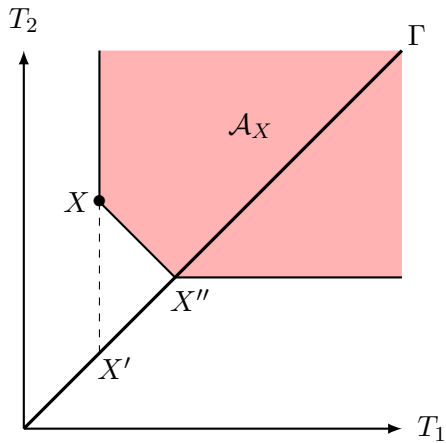
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- Rubbing each of the copper pieces.

- Heat conduction through the connecting layer.

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The 'forward sector' $\mathcal{A}_X = \{Y : X \prec Y\}$ of $X = (T_1, T_2)$ then consists of all points that can be obtained by rubbing, starting from any point on the line segment between (T_1, T_2) and the equilibrium point $(\frac{1}{2}(T_1 + T_2), \frac{1}{2}(T_1 + T_2))$.

A toy example (cont.)

As equilibrium entropy we take $S(T, T) = \log T$.

The points X' and X'' are

$$X' = (\min\{T_1, T_2\}, \min\{T_1, T_2\}) \qquad X'' = (\tfrac{1}{2}(T_1 + T_2), \tfrac{1}{2}(T_1 + T_2))$$

and hence

$$S_-(T_1, T_2) = \min\{\log T_1, \log T_2\} \qquad S_+(T_1, T_2) = \log(\tfrac{1}{2}(T_1 + T_2)).$$

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Extending the relation $\prec$ by allowing separation of the pieces and reversible thermal equilibration restores CP and leads to the unique entropy

$$S(T_1, T_2) = \tfrac{1}{2}(\log T_1 + \log T_2)$$

This corresponds to the framework of Classical Irreversible Thermodynamics (CIT) where the global state is determined by local equilibrium variables.

A toy example (cont.)

However, when heat conduction does not obey Fourier's law but rather a hyperbolic equation as in Cattaneo's law it is necessary to introduce the heat fluxes as a new independent variables and apply Extended Irreversible Thermodynamics (EIT).

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An entropy depending explicitly on the fluxes can be introduced and this entropy behaves in some respects better than the CIT entropy that is not monotone under heat conducetion. The numerical equality of the extended entropy with the entropy of some equilibrium state does, however, not imply that the state with a flux and the equilibrium state are adiabatically equivalent.
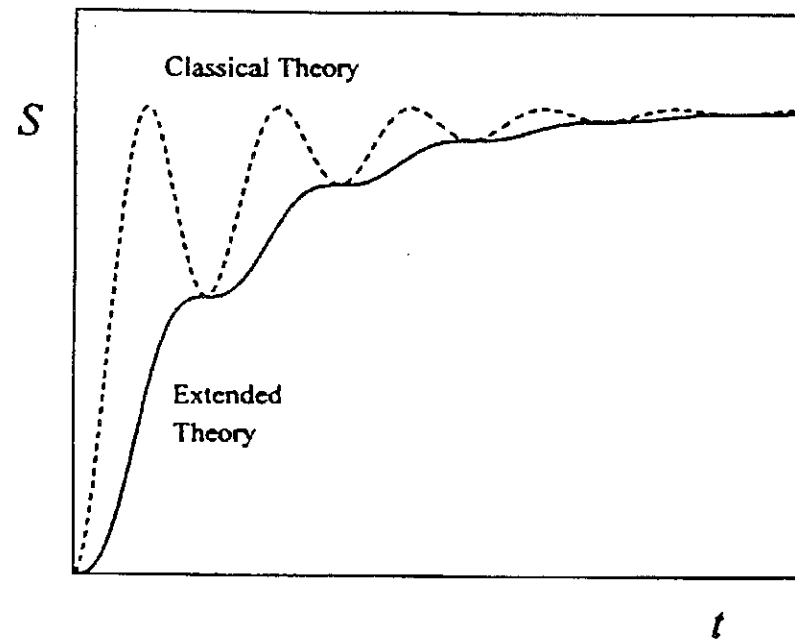
Fig. 7.2 The evolution of the classical entropy S_{CIT} during the equilibration of an isolated system when use is made of Cattaneo's equation is given by the *dashed curve*. The evolution of the extended entropy S_{EIT}, obtained from (7.2.15), is represented by the *solid curve*, which, in contrast with that of S_{CIT}, increases monotonically

Summary and Conclusions

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2. Comparability is a highly nontrivial property. Even in the the equilibrium situation it requires additional assumptions beyond A1-A6.

3. It is implausible to postulate comparability for arbitrary non-equilibrium states.

4. It is, however, always possible to delimit the range of adiabatic state changes by means of two well defined entropy functions. Comparability holds if and only if these two functions coincide.