As mentioned earlier, the existence of entropy leads to surprising relations between quantities that at first sight look unrelated since they are measured with very different means and do not involve entropy directly. Examples:

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

We shall now discuss these examples. For the last two we shall introduce and make use of the important concepts of **free energy** and **chemical potentials**.

7. VELOCITY OF SOUND

From fluid dynamics it is known that the velocity of sound, v_{sound}, is given by

$$v_{\text{sound}}^2 = \left(\frac{\partial P}{\partial \rho}\right)_S$$

where

$$\rho = \frac{n \cdot m}{V}$$

is the mass density.

By the formula for the entropy of an ideal gas we have at constant entropy

$$\text{const.} = T^{C_V} \cdot V^{nR}$$

which, with $PV = nRT$, gives

$$PV^{\gamma} = \text{const.}$$

where

$$\gamma := \frac{C_V + nR}{C_V}.$$

Now

$$\left(\frac{\partial P}{\partial \rho}\right)_S = -\frac{V^2}{mn}\left(\frac{\partial P}{\partial V}\right)_S$$

and

$$\left(\frac{\partial P}{\partial V}\right)_S = -\gamma V^{-\gamma-1}(PV^\gamma) = -\gamma\,\frac{P}{V}$$

so

$$v_{\text{sound}}^2 = \left(\frac{\partial P}{\partial \rho}\right)_S = \gamma\frac{PV}{mn} = \gamma\frac{RT}{m}.$$

The numerator, $C_V + nR$, of γ is nothing but the the heat capacity, C_P, at constant pressure:

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P = T\left[\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P\right] = C_V + nR.$$

We can thus also write the formula as

$$\frac{mv^2_{\text{sound}}}{RT} = \frac{C_P}{C_V}.$$

8. THERMODYMIC POTENTIALS

We have seen that the entropy S as a function of its natural variables (U, V) is a **thermodynamic potential,** i.e., it yields the caloric and thermal equations of state upon differentiation. In practice, it is often more convenient to use other variables than (U, V), in particular (T, V) or (T, P).

Define the (Helmholz) **Free Energy** as

$$F = U - TS$$

For a simple system have

$$dF = dU - TdS - SdT = TdS - PdV - TdS - SdT,$$

i.e

$$dF = -SdT - PdV$$

which means that

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \quad \text{and} \quad P = -\left(\frac{\partial F}{\partial V}\right)_T .$$

The latter is the thermal equation of state. The caloric equation is given by

$$U(T,V) = F(T,V) + T \left(\frac{\partial F}{\partial T}\right)_V .$$

Like U, S and V the free energy is extensive, i.e., if we include the mole number n as variable,

$$F(T,V,n) = n f(T,v)$$

with

$$f = F/n \quad \text{and} \quad v = V/n.$$

It is also **additive**, for composed systems, **provided all subsystems have the same temperature**,

$$F(T, V_1, \dots, V_K, n_1, \dots, n_K) = \sum_i F_i(T, V_i, n_i).$$

Consider now a system together with a thermal reservoir at temperature T. In any process within this closed, combined system we have, by the second law,

$$\Delta S + \Delta S_{\text{res}} \geq 0.$$

Moreover, $\Delta S_{\text{res}} = \Delta U_{\text{res}}/T$, and $\Delta U_{\text{res}} = -\Delta U$ (by the First Law). Hence $\Delta S - \Delta U/T \geq 0$.

This can also be written

$$\Delta F \leq 0.$$

We conclude that under the stated conditions the free energy can only decrease, so **the free energy is at minimum in equilibrium at fixed temperature**.

Another important thermodynamic potential is the **Gibbs Free Energy**

$$G = F + PV = U - TS + PV.$$

The fundamental equation in terms of G is

$$dG = -SdT + VdP$$

i.e.

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \quad \text{and} \quad V = \left(\frac{\partial G}{\partial P}\right)_T .$$

The natural variables of G are thus (T, P). For simple systems G is extensive:

$$G(T, P, n) = ng(T, P).$$

For compound systems G is additive, provided all subsystems have the same temperature and pressure:

$$G(T, P, n_1, \dots, n_K) = \sum_i n_i \, g_i(T, P).$$

Consider now a system together with a thermal reservoir at temperature T and a work reservoir (weight) maintaining a pressure P. In any process in this closed compound system the we have, by the first and second laws

$$\Delta U + \Delta U_{\mathrm{res}} + \Delta U_{\mathrm{weight}} = 0 \quad , \quad \Delta S + \Delta S_{\mathrm{res}} \geq 0.$$

With

$$\Delta U_{\text{weight}} = P\Delta V, \qquad \Delta S_{\text{res}} = \frac{\Delta U_{\text{res}}}{T} = \frac{-\Delta U - P\Delta V}{T},$$

we obtain

$$\Delta G \leq 0.$$

We conclude that under the stated conditions the Gibbs free energy can only decrease, so **the Gibbs free energy is at minimum in equilibrium at fixed temperature and pressure**.

9. THE CLAUSIUS-CLAPEYRON EQUATION

We can apply the minimum principle for the Gibbs free energy to state the condition for two **phases** of a substance, e.g. liquid and gas, to be in equilibrium with each other.

Let $g_1(T, P)$ and $g_2(T, P)$ be the molar Gibbs free energies for the two phases.

The Gibbs free energy of one mole of the substance, divided in a ratio x to (1-x) between the phases, is

$$xg_1(T,P) + (1-x)g_2(T,P)$$

In equilibrium this must be minimal with respect to variations of x, so the **equilibrium condition** is

$$g_1(T,P) = g_2(T,P).$$

This determines the pressure $P = P(T)$ at the **coexistence curve** in a (T,P) diagram.

Differentiating w.r.t. T gives

$$\frac{d}{dT} g_1(T, P(T)) = \frac{d}{dT} g_2(T, P(T))$$

which, because $(\partial g/\partial T) = -s$ and $(\partial g/\partial P) = -v$, gives

$$\frac{dP(T)}{dT} = \frac{\Delta s}{\Delta v}$$

with $\Delta s = s_1 - s_2$, $\Delta v = v_i$, the s_i and v_i being respectively the molar entropies and volumina of the two phases.

Usually one employs that $\Delta s = \frac{\Delta h}{T}$ where Δh is the **latent heat** of the phase transition.This is the same as $h_1 - h_2$ with

$$h = u + Pv$$

being the molar **enthalpy**.

Then the **Clausius -Clapeyron equation** takes the form

$$\frac{dP(T)}{dT} = \frac{\Delta h}{T \Delta v}.$$

10. CHEMICAL POTENTIALS

A **mixture** of different substances is not a compound systems in the sense of the earlier definition, and its Gibbs free energy

$$G(T, P; n_1, \ldots, n_K)$$

may depend nontrivially on all the mole numbers n_i. The equilibrium condition for two mixtures to be in equilibrium w.r.t. exchange of one of the substances, say i, is that

$$G^{(1)}(T,P;n_1^{(1)},\ldots,n_K^{(1)})+G^{(2)}(T,P;n_1^{(2)},\ldots,n_K^{(2)})$$

is at minimum with respect to a variations of $n_i^{(1)}$ and $n_i^{(2)}$ with $n_i^{(1)}+n_i^{(2)}$ fixed.

This means that

$$\mu_i^{(1)}=\mu_i^{(2)}$$

where

$$\mu_i := \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}}$$

is the **chemical potential** of substance i in the mixture.

For a single substance $G(T, P., n) = n\, g(T, P)$ so in that case the chemical potential is nothing but the molar Gibbs free energy and the equilibrium condition is the same as the one derived before.

For an **ideal gas** it follows from the formula for entropy and the equation of state that

$$\mu = RT \ln \frac{P}{P_0} + g^0(T)$$

while for a **mixture of ideal gases** it can be argued that

$$\mu_i = RT \ln \frac{P_i}{P_0} + g_i^0(T)$$

with

$$P_i = \frac{n_i}{n_{\text{tot}}} P$$

the **partial pressure** of substance i.

The equation for a **chemical reaction** can always be written as

$$0 \rightleftharpoons \nu_1 A_1 + \cdots + \nu_{k+l} A_{k+l}$$

where the A_j are the chemical substances involved and the $\nu_j \in \mathbb{Z}$ the **stoichiometrical coefficients**. The minimum principle for the Gibbs free energy implies the equilibrium condition

$$\sum_j \nu_j \mu_j = 0.$$

For a reaction in a mixture of ideal gases this leads immediately to the **Law of Mass Action**:

$$K_{\mathsf{P}} := \prod_{i=1}^{l+k} \left(\frac{P_i}{P_0} \right)^{\nu_i}$$

is a function of T alone, independent of the total pressure and the mole numbers, namely

$$K_{\mathsf{P}}(T) = e^{-\frac{\Delta G^0(T)}{RT}}$$

with

$$\Delta G^0(T) := \sum_j \nu_j g_j^0(T).$$

We can also derive the **van’t Hoff equation**:

Because $\left(\frac{\partial G}{\partial T}\right)_P = -S$ we have $\frac{d}{dT}\Delta G^0 = -\Delta S^0$. and

$$\frac{d}{dT}\ln K_{\mathsf{P}}(T) = \frac{\Delta H^0}{RT^2}$$

where ΔS^0 is the entropy change in the reaction and $\Delta H^0 = \Delta G^0 + T\,\Delta S^0$ the **heat of reaction**.

STATISTICAL MECHANICS

Statistical mechanics provides recipies for computing thermodynamic potentials from assumptions about the microscopic properties of the system.

In classical statistical mechanics the formula for the entropy of N particles in a volume V with total energy U is

$$S = k \ln \Omega$$


S = k. log W
LUDWIG
BOLTZMANN
1844 – 1906
HENRIETTE
OLTZMANN
EDLE VON AIGENTLER
1854 – 1938
DR PHIL. PAULA
BOLTZMANN
GEB. CHIARI
1891 – 1977
ARTHUR
BOLTZMANN
DIPL. ING. DR PHIL. HOFRA
1881 – 1952
LUDWIG
BOLTZMAN
1923 – 1943
LETZTER MÄNNLICHER NACHKO
GEFALLEN BEI SMOLENS

where

$$\Omega = \text{volume of phase space with energy} \leq U$$

For indistinguishable particles the phase space volume should be divided by $N!$

This method is said to be that of the **micro-canonical ensemble**.

Example: **Ideal 3D monoatomic gas**, hamiltonian

$$H(\mathbf{p},\mathbf{q}) = \frac{|\mathbf{p}|^2}{2m}$$

With Stirlings formula this gives for large N

$$\Omega = (\text{const.})^N (V/N)^N (U/N)^{3N/2}$$

and hence

$$S(U,V,N) = Nk\left[\frac{3}{2}\ln\frac{U}{N} + \ln\frac{V}{N} + \text{const.}\right].$$

The **canonical ensemble** gives a formula for the **free energy**: Define the canonical partition function as

$$Z = \int \text{exp}(-H(\mathbf{p},\mathbf{q})/kT)d\mathbf{p}d\mathbf{q}$$

(divided by $N!$ for indistinguishable particles).

Then the free energy is given by

$$F = -kT \ln Z$$

For the **ideal gas**

$$Z = (N!)^{-1} Z_1^N$$

with

$$Z_1 = V \int_{\mathbb{R}^3} \text{exp}(-p^2/2mkT) d^3p = (\text{const.})(mkT)^{3/2}.$$

This gives the same formula for the entropy as before in the **thermodynamic limit** $N \to \infty$, $V \to \infty$, N/V fixed.

ENTROPY FOR NON-EQUILIBRIUM STATES

General remarks:

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

- The role of Entropy is less prominent than in equilibrium thermodynamics.

Consider a system with a space Γ of **equilibrium** states that is a subset of some larger space $\widehat{\Gamma}$ of **non-equilibrium** states.

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

Basic question: What are the **possible extensions** of S to $\widehat{\Gamma}$ that are monotone w.r.t. $\prec$?

Assumption for the nonequilibriums states

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).

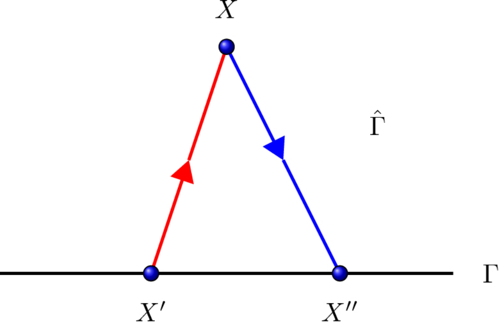
N2. For every $X \in \hat{\Gamma}$ there are $X', X'' \in \Gamma$ such that $X' \prec X \prec X''$.

Definition of non-equilibrium entropies

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

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

Thus S_- measures how large the entropy can be of an equilibrium state out of which X is created by an adiabatic process, and S_+ measures how small the entropy of an equilibrium state can be into which X equilibrates by an adiabatic process.


X
$\hat{\Gamma}$
Γ
X'
X''

.

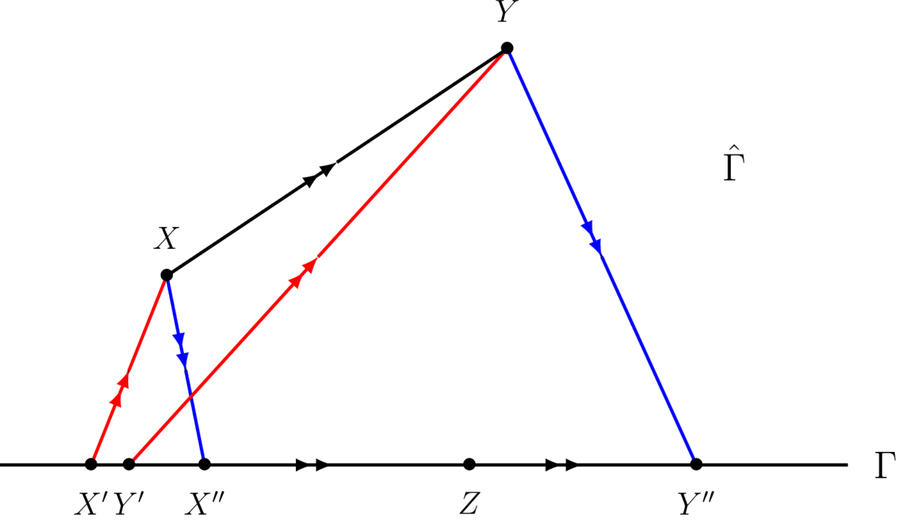
Remark. The stability assumption implies that the sup and inf are attained at some states $X', X'' \in \Gamma$.

PROPOSITION

(1) Both S_- and S_+ are monotone with respect to $\prec$.

(2) Any other function $\widehat{S}$ on $\widehat{\Gamma}$ that has this property and coincides with S on Γ lies between S_- and S_+.

(3) If $S_+(X) \prec S_-(Y)$ then $X \prec Y$.


Y
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X
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X'
Y'
X''
Z
Y''

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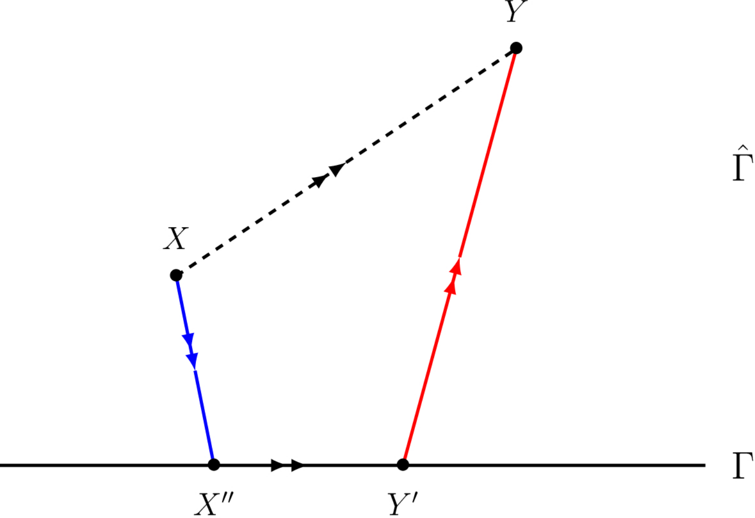
Y
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X
Γ
X''
Y'

.

Proof. (1) If $X \prec Y$, then $X' \prec X \prec Y \prec Y$”, so by transitivity $X' \prec Y$ and $X \prec Y$”. By the definition of $S_\pm$ this implies

$$S_-(X) = S(X') \leq S_-(Y) \quad \text{and} \quad S_+(X) \leq S(Y) = S_+(Y).$$

(2) Let $\widehat{S}$ be another monotone function w.r.t. $\prec$ coinciding with S on Γ. Then

$$\begin{aligned} S_-(X) = S(X') = \widehat{S}(X') \leq \widehat{S}(X) \\ \leq \widehat{S}(X'') = S(X'') = S_+(X). \end{aligned}$$

(3) If If $S_+(X) \leq S_-(Y)$ then $X'' \prec Y'$, and thus $X \prec X'' \prec Y' \prec Y$, which implies $X \prec Y$ by transitivity.

$\square$

Two further properties of $S_\pm$ have only slightly more complicated proofs:

(4) Under composition, S_- is superadditive and S_+ subadditive.

(5) The available energy (exergy) of a state $X \in \hat{\Gamma}$ *satisfies*

$$(U-U_0)-T_0(S_+-S_0) \leq \Phi(X) \leq (U-U_0)-T_0(S_--S_0).$$

Proof of (5): Let $X_0 \in \Gamma$ be the "dead" final state with temperature T_0, energy U_0 and entropy S_0. Consider the process $X \to X'' \to X_0$. The work obtained in the step $X \to X''$ is $U - U''$. In the step $X'' \to X_0$ the maximum work (by the previous reasonings for equilibrium states in Γ) is $(U'' - U_0) - T_0(S(X'') - S_0)$.

Altogether, using that $S(X'') = S_+$, we have

$$\begin{aligned}\Phi(X) &\geq U - U'' + (U'' - U_0) - T_0(S_+ - S_0) \\ &= (U - U_0) - T_0(S_+ - S_0).\end{aligned}$$

An analogous reasoning applied to $X' \to X \to X_0$ gives

$$\Phi_{X_0}(X') = U' - U_0 - T_0(S_- - S_0) \geq U' - U + \Phi_{X_0}(X)$$

and hence

$$\Phi_{X_0}(X) \leq (U - U_0) - T_0(S_- - S_0).$$

THEOREM (Role of comparability). *The following are* **equivalent***:*

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

(ii) There exists a **unique** $\widehat{S}$ *extending* S *such that* $X \prec Y$ *implies* $\widehat{S}(X) \leq \widehat{S}(Y)$*.*

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

(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 comparable with every $Z \in \Gamma$.

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

Proof. That (i) is equivalent to (ii) follows from the statements (1) and (2) of the Proposition. Moreover, (ii) implies (iii) by (3).

(v) → (ii): If $S(X') = S_-(X) < S_+(X) = S(X'')$ there exists a $Z \in \Gamma$ with $S(X') < S(Z) < S(X'')$. If (v) holds, then either $Z \prec X$ or $X \prec Z$. The first possibility contradicts the definition of S_- and the latter definition of S_+. Hence $S_- = S_+$, so (v) implies (ii).

It is clear that (vi) → (v) because CP holds on Γ.

Finally, (ii) $\rightarrow$ (vi): Since $X', X'' \in \Gamma$, and $S(X') = S(X'')$ (by (ii)), we know that $X' \overset{\mathrm{A}}{\sim} X''$, because the entropy S characterizes the relation $\prec$ on Γ by assumption. Now $X' \prec X \prec X''$, so $X \overset{\mathrm{A}}{\sim} X' \overset{\mathrm{A}}{\sim} X''$. $\square$

We now address the question whether one of the equivalent conditions of the Theorem, in particular (vi), which demands that every **non-equilibrium state** under consideration is **adiabatically equivalent** to an **equilibrium state**, can be proved to hold in concrete situations.

Stated in other words, the condition requires the operating physicist to bring a non-equilibrium state so ”gently” to equilibrium that the non-equilbrium state can again be completely restored by an adiabatic operation. Certainly a difficult task!

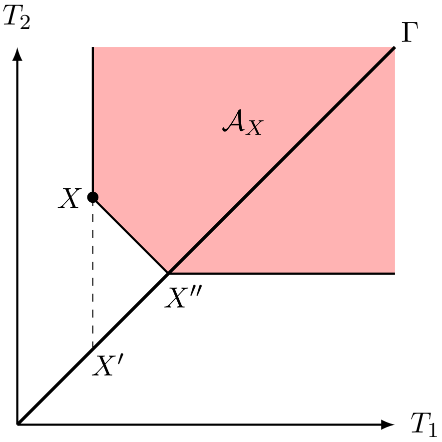
To discuss this question it is instructive to consider a very simple “toy model” that captures some salient features of the problem.

A TOY MODEL

The system consists of two identical silver coins 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 coins. 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, $T_1 = T_2$.

Assume to begin with that the relation $\prec$ is defined by the following 'restricted' adiabatic operations:

- Rubbing each of the coins.
- Heat conduction through the connecting layer.


T_2
Γ
$\mathcal{A}_X$
X
X''
X'
T_1

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 $(\frac{1}{2}(T_1 + T_2), \frac{1}{2}(T_1 + T_2))$.

As equilibrium entropy on the diagonal Γ we take

$$S(T, T) = \log T.$$

The points X' and X'' are

$$\begin{aligned} X' &= (\min\{T_1, T_2\}, \min\{T_1, T_2\}) \\ X'' &= (\tfrac{1}{2}(T_1 + T_2), \tfrac{1}{2}(T_1 + T_2)) \end{aligned}$$

and hence

$$\begin{aligned} S_-(T_1, T_2) &= \min\{\log T_1, \log T_2\} \\ S_+(T_1, T_2) &= \log(\tfrac{1}{2}(T_1 + T_2)). \end{aligned}$$

It is clear that **CP does not hold** for **this** relation.

Extending the relation to another relation by allowing separation of the pieces and **reversible** thermal equilibration **restores CP** and leads to the **unique entropy**

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

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

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

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 conduction.

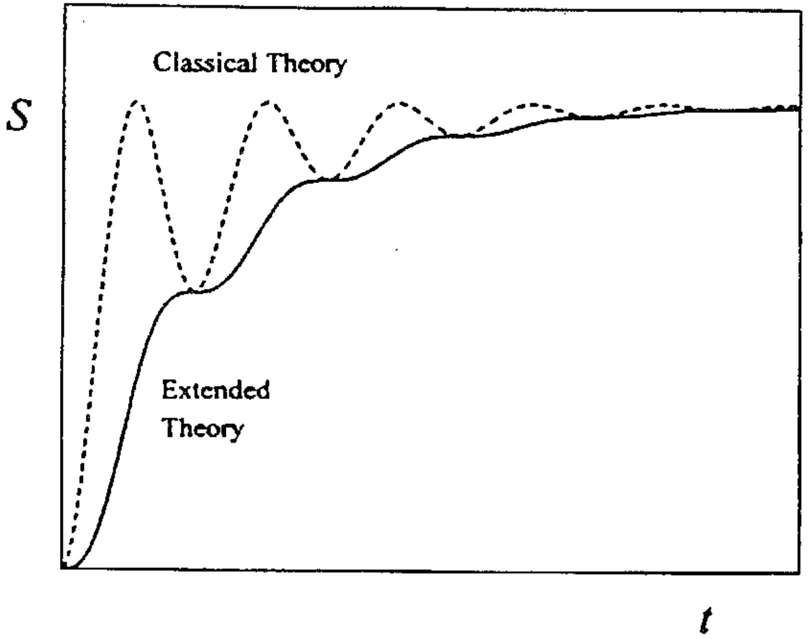


Fig. 7.2 The evolution of the classical entropy S_{CIT} during the equilibration of an isolated system when use is made of Cattaneo's equation is given by the *dashed curve.* The evolution of the extended entropy S_{EIT}, obtained from (7.2.15), is represented by the *solid curve*, which, in contrast with that of S_{CIT}, increases monotonically

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.

We conclude that it is **highly inplausibe** that the CP property and the corresponding existence of a **unique** entropy holds **in general**.

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SUMMARY

In these lectures we have

1. Defined and discussed the properties of **entropy for equilibrium states**, based entirely on the **relation of adiabatic accessibility**.

2. Described some important and nontrivial applications of entropy, introducing concepts like **free energy** and **chemical potentials** on the way.

3. Briefly sketched connections to **equilibrium statistical mechanics**.

4. Disussed the possibilities for defining an **entropy for non-equilibrium states** with the conclusion that a unique entropy can **not** be expected to exist for such states **in general**.