Chapter 2

Thermodynamics

2.1 Description of thermodynamic states and transformations

2.2 Introductory remarks and basic definitions

Thermodynamics is a phenomenological theory in contrast to the microscopic theories considered so far, i.e. it does not refer to the microscopic, quantum mechanical behavior of matter, but is based on the observation of the macroscopic properties of "large" systems and the relations among these properties, where "large" requires further specification.

As a result, thermodynamics cannot make absolute statements derived from microscopics, but can only describe the dependence of macroscopic properties on each other. Any definition of a new quantity not known outside of thermodynamics, like temperature T, entropy S, must therefore be *implicit* through these dependencies. This leaves some sense of "incompleteness" , like in any phenomenological theory.

On the other hand, because it does not rely on detailed microscopic properties or assumptions, thermodynamics is completely *general* and closed in itself. It is the strength of thermodynamics that it is applicable to a *vast variety of systems.*

Einstein about thermodynamics

> "Eine Theorie ist desto eindrucksvoller, je größer die Einfachheit ihrer Prämissen ist, je verschiedenartigere Dinge sie verknüpft und je weiter ihr Anwendungsbereich ist. Deshalb der tiefe Eindruck, den die klassische Thermodynamik auf mich machte. Es ist die einzige physikalische Theorie allgemeinen Inhalts, von der ich überzeugt bin, dass sie im Rahmen der Anwendbarkeit ihrer Grundbegriffe niemals umgestoßen werden wird."

Thermodynamics has been developed during the 19th century, driven by the need to understand thermodynamic cyclic processes and to develop heat engines that were able to transform heat into mechanical work. Therefore, the central definitions of thermodynamics have an operational character, i.e. are derived from cyclic processes.

Thermodynamics is based on our every-day observation that most macroscopic systems, when left to themselves, reach after a sufficiently long time a steady state, in which the macroscopically observable quantities don't change in time. These states are called *"equilibrium states"*. In the present course we will consider only thermodynamic equilibrium states and transitions between them. The statements made above can be quantified by the following basic definitions:

- *Thermodynamic system:* Any macroscopic system consisting of N equal entities (e.g. particles, magnetic moments (spin)...) with $\sqrt{N} \gg 1$.
  (See statistical mechanics for the relevance of the square root.)
- A *thermodynamical state* is a state of the system which is completely determined by a set of macroscopic *thermodynamic state variables.*
- A *state variable* X is a physical quantity characterized by the fact that a thermodynamic state is uniquely determined by specifying the value of X and it *does not depend on the history* by which this state has been reached.

  In other words: If the thermodynamic state of a system is changed, the amount by which a state variable changes is independent of the path in parameter space taken for this change. For a non-state variable the change will, in general, depend on the the path. This distinguishes state variables from non-state variables.

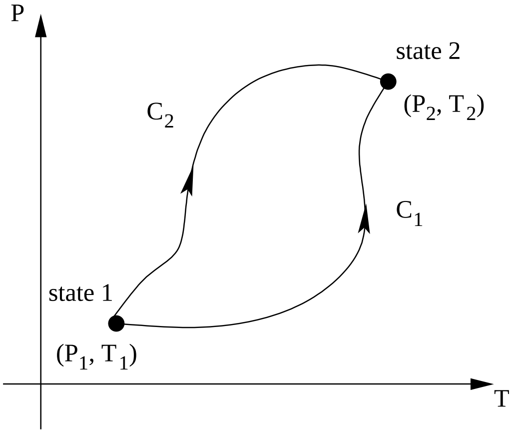

Figure 2.1: A gas undergoing temperature, volume and pressure change

Examples:

- pressure p
- volume V
- temperature T
- particle number N
- chemical potential μ (defined later)
- magnetic field $\vec{B}$
- magnetization $\vec{\mu}$
- electric field $\vec{E}$
- electric polarization $\vec{P}$

are *state variables*, but "heat" Q is not a state variable.

- One distinguishes intensive and extensive quantities:
  - *intensive:*
    volume $V \to \alpha V: \quad x(\alpha V) = x(V)$
    x is invariant under scaling of the system volume
  - *extensive:*
    volume $V \to \alpha V: \quad x(\alpha V) = \alpha x(V)$
    x scales with the system volume

- *Thermodynamic equilibrium:*
  State in which the state variables do not change with time.
- The functional relation between all the (relevant) state variables in equilibrium is called *equation of state*: $f(P, V, N, T) = 0$

  E.g. for the ideal gas:

  $$\boxed{pV = Nk_BT} \tag{2.1}$$

  Equations of state will be considered in more detail later.

  Thermodynamic changes of state:

  1. *quasistatic:*
     slow change, so that the system remains (nearly) in equilibrium during the change for each momentary set of state variables.
  2. *reversible:*
     system returns to its initial state upon time reversal (i.e. by running all processes as under reversed time). Entropy change $\Delta S = 0$, see below.
  3. *irreversible:*
     system does not return to its initial state upon time reversal, $\Delta S > 0$.
  4. *isothermal:*

     $$\Delta T = 0 \tag{2.2}$$

  5. *adiabatical:*

     $$\Delta Q = 0 \tag{2.3}$$

     process without heat exchange
  6. *isobar:*

     $$\Delta P = 0 \tag{2.4}$$

7. *isochor:*

$$\Delta V = 0 \tag{2.5}$$

- A heat bath is a system (heat reservoir) which is large compared to the system under consideration, and which is kept at constant temperature T.

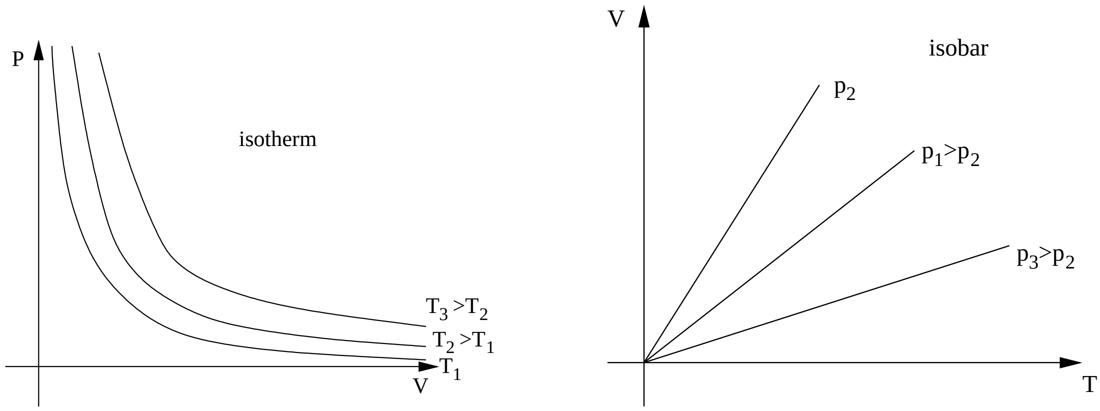

Figure 2.2: Examples for a change of state of an ideal gas

Note: These examples preclude the quantity T which will be defined only below.

2.3 State variables and exact differentials

The definition of a state variable (independence of path) can be put in mathematical terms:

Let $F(x_1, \ldots, x_n)$ be a function of the variables $x_1, \ldots, x_n$. The differential of F is

$$dF = \sum_{i=1}^{n} \left(\frac{\partial F}{\partial x_i} \right)_{\{x_{j \neq i}\}} dx_i \tag{2.6}$$

Partial derivative of F with respect to x_i, keeping all $x_j, j \neq i$, fixed.

If the $\{x_i\}$ are state variables, then the partial derivatives commute:

$$\left[\frac{\partial}{\partial x_k} \left(\frac{\partial F}{\partial x_i} \right)_{\{x_{j \neq i}\}} \right]_{\{x_{l \neq k}\}} = \left[\frac{\partial}{\partial x_i} \left(\frac{\partial F}{\partial x_k} \right)_{\{x_{l \neq k}\}} \right]_{\{x_{j \neq i}\}} , \qquad i, k = 1, \ldots, n \tag{2.7}$$

$$\left[\text{For 2 variables: } \left[\frac{\partial}{\partial x_2}\left(\frac{\partial F}{\partial x_1}\right)_{x_2}\right]_{x_1} = \left[\frac{\partial}{\partial x_1}\left(\frac{\partial F}{\partial x_2}\right)_{x_1}\right]_{x_2}.\right]$$

For a non-state variable the partial derivatives do not commute in general.
If the partial derivatives commute 2.7, then dF (equation 2.6) is called *exact differential.*

Macroscopic consequence of commuting partial derivatives:

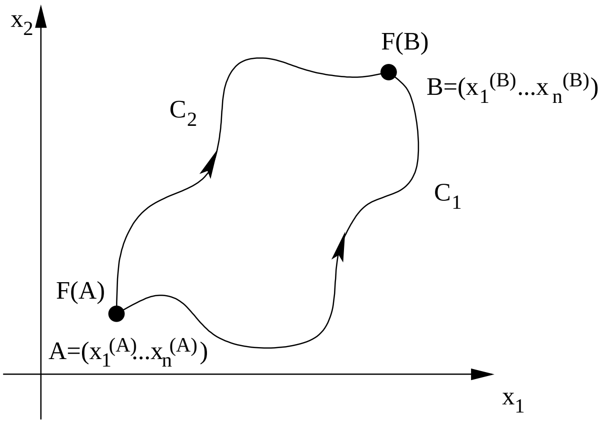

Figure 2.3: Independence of a thermodynamic state change on the path taken

Independence of the path taken:

$$F(B) - F(A) = \int_A^B dF = \int_{C_1}\left[\sum_{i=1}^{n}\left(\frac{\partial F}{\partial x_i}\right)_{\{x_{j\neq i}\}} dx_i\right] \tag{2.8}$$

$$= \int_{C_2}\left[\sum_{i=1}^{n}\left(\frac{\partial F}{\partial x_i}\right)_{\{x_{i\neq j}\}} dx_i\right] \tag{2.9}$$

The property that the differentials of all state variables are *exact* implies interesting relations between the state variables for a path for which $F(x_1, \ldots, x_n) = 0$, which are purely founded in this mathematical structure, and which are therefore very general.

Let x, y, z, w be state variables, $F(x, y, z, w) = 0$.

$$\begin{aligned}
\left(\frac{\partial x}{\partial y}\right)_z &= \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} && (2.10)\\
\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y &= -1 && (2.11)\\
\left(\frac{\partial x}{\partial w}\right)_z &= \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial w}\right)_z && (2.12)\\
\left(\frac{\partial x}{\partial y}\right)_z &= \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z && (2.13)
\end{aligned}$$

Proof of 2.10 and 2.11:

$$\begin{aligned}
F(x, y, z) &= 0 && (2.14)\\
x &= x(y, z), \qquad y = y(x, z) && (2.15)\\
dx &= \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \qquad (*) && (2.16)\\
dy &= \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \qquad \text{in}\,(*): && (2.17)\\
dx &= \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz && (2.18)
\end{aligned}$$

varying x, z independently:

$$\begin{aligned}
\left(\frac{\partial x}{\partial y}\right)_z &= \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} && (2.19)\\
\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y &= -1 && (2.20)
\end{aligned}$$

Although these relations follow trivially from any function of multiple variables with exact differential, they imply useful relations between the state variables which can be used in describing state changes.

Summary of thermodynamic concepts

- Thermodynamical (equilibrium) state:
  Stationary state of a system with many degrees of freedom (particles, spins, …) which is reached after suffiently long time, if there is no external action on the system. (Only equilibrium states considered here.)

- State variable:
  Physical quantity which has a *unique* value for a given thermodynamic state. A complete set of state variables determines a thermodynamic state uniquely.

- State equation:

  $$F(p, V, N, T, \ldots) = 0 \tag{2.21}$$

  Relation between state varibales for a given system.

- Mathematical characterization of state variables X, Y
  Partial derivatives of F wrt. X, Y commute,

  $$\left[\frac{\partial}{\partial Y}\left(\frac{\partial F}{\partial X}\right)_Y\right]_X = \left[\frac{\partial}{\partial X}\left(\frac{\partial F}{\partial Y}\right)_X\right]_Y \tag{2.22}$$

  for any pair X, Y, i.e. F has an *exact* differential wrt. X, Y:

  $$dF = \left(\frac{\partial F}{\partial X}\right)_Y dX + \left(\frac{\partial F}{\partial Y}\right)_X dY \tag{2.23}$$

  This implies that the values of X, Y in a thermodynamic state A is independent of the path by which A has been reached.

2.4 The fundamental laws of thermodynamics

2.4.1 The first law: energy conservation

In any change of state the change of the total energy of a system (=internal energy U) is equal to the energy added to the system, minus the energy extracted.

We express the change dU during an infinitesimal state change in terms of the changes of the *extensive* variables:

– Mechanical work done by the system:

$$-dW = -\vec{F} \cdot d\vec{x} = -\frac{F}{A} \cdot (A\, dx) = -p\, dV \tag{2.24}$$

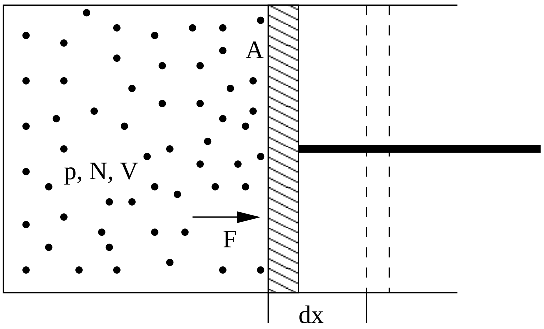

Figure 2.4: Mechanical work

– Change of energy due to increase of particle number:

$$\mu\, dN \qquad \mu = \text{chemical potential} \\ = \text{change of energy due to adding one particle} \tag{2.25}$$

– Heat is a form of energy (undirected motion of particles).

$$dQ \qquad Q \text{ is extensive, but not a state variable,} \\ \text{as will be seen below} \tag{2.26}$$

The energy conservation is then written in terms of the extensive variables (infinitesimal state change):

$$\boxed{dU = dQ - pdV + \mu dN} + \text{(possibly other variables)} \tag{2.27}$$

For an infinitesimal state change, the law of energy conservation is then written in terms of the *extensive* variables as

$$\boxed{dU = dQ - p\,dV + \mu\,dN} \tag{2.28}$$

1st law of thermodynamics. U is state variable.

2.4.2 The second law of thermodynamics: Heat and the state variables temperature T and entropy S

We have an intuitive concept of "hot" and "cold", which is a *unique* property of a thermodynamic state, i.e. corresponds to a state variable.
It is clear that "heat", as an amount of energy, is *not* a state variable, because we can add a given amount of heat energy (e.g. by burning a fixed amount of gasoline) to a cold body as well as to a hot body. This means that heat does not characterize the state of a system uniquely.
Therefore, we need to look for a different state variable quantifying the property "hot" or "cold". This leads to the quantity temperature T and at the same time to the concept of the state variable entropy S.
The definition of T is (and has to be !) operational, i.e. through the dependence of other state variables on T.

Basic statement for the definition of temperature:
Two thermodynamic systems which are in heat contract (i.e. can freely exchange heat) are at the same temperature (after sufficiently long time). This means that temperature can be defined for a specific, conveniently chosen system. The temperature of any system can then be determined by comparison (heat contract) with the reference system. This is the basis for any thermometer.

(a) **The ideal gas thermometer (ideal gas T scale)**

The equation of state for an ideal gas (sufficiently dilute so that atomic interactions are negligible) is known experimentally:

$$p = \frac{\alpha(N,T)}{V} \tag{2.29}$$

where the proportionality constant α depends on the particle number N of the gas,

$$\alpha \sim N \tag{2.30}$$

and on the property how "hot" the gas is. The hotter the gas, the bigger α.

We *define* the temperature T through the simplest possible, monotonically increasing dependence of α on T.

$$\alpha \sim T \tag{2.31}$$

We then have

$$\alpha = N k_B T \tag{2.32}$$

and the ideal gas law

$$pV = N k_B T. \tag{2.33}$$

The universal proportionality constant k_B has units [energy/temperature] and is called Boltzmann constant.

The ideal gas law implies that there is an absolute zero point of T, since $pV \geq 0$.

The numerical value of k_B depends on the scale chosen for the temperature T.

Convention:

The temperature interval between the freezing and the boiling point of water at atmospheric pressure corresponds to 100 degrees Kelvin, 100K (**Kelvin scale**).

In these units the freezing point of H_2O is at 273,15K, and k_B takes the value:

$$\boxed{k_B = 1,38 \cdot 10^{-23} \frac{J}{K}} \quad \text{Boltzmann constant} \tag{2.34}$$

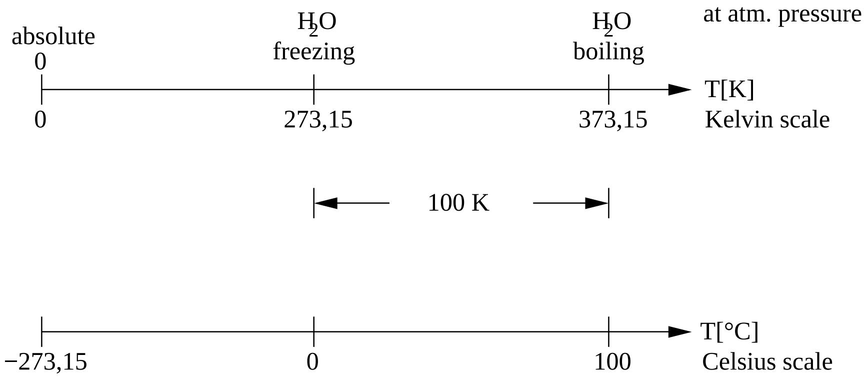

Figure 2.5: Temperature scales

The conventions

$$\left.\begin{array}{l} -\ \alpha \sim T, \quad \text{i.e. } T_0 = 0 \text{ and} \\ -\ T_{\text{boil}} - T_{\text{freeze}} = 100K \end{array}\right\} \text{Kelvin scale}$$

determine the temperature T uniquely as a state variable and give a prescription how to measure it via the ideal gas law.

Celsius scale:

$$T_{\text{boil}}^{\text{Celsius}} - T_{\text{freeze}}^{\text{Celsius}} = 100\,C \tag{2.35}$$

$$T_{\text{freeze}}^{\text{Celsius}} = 0\,C \tag{2.36}$$

($T_0^{\text{Celsius}} = -273,15\,C$ and $\alpha = T^{\text{Celsius}} + 273.15\,C$)

For convenience, we will use the Kelvin scale only.

(b) The second law of thermodynamics

Through numerous observations of processes in nature it has been established empirically:

There does not exist any thermodynamic change of state, whose *only* consequence is that

(1) an amount of heat is taken from a heat reservoir and is completely transferred into mechanical work, or

(2) an amount of heat is taken from a colder heat reservoir and given to a warmer heat reservoir.

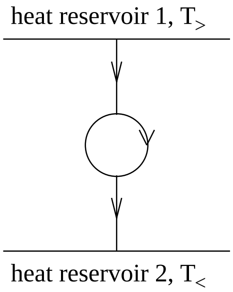

Figure 2.6: A heat engine working between two heat reservoirs 1, 2

For the further considerations we define:

A **Thermodynamic or heat engine** is a cyclic process, where

(1) a working system takes up an amount of heat $Q_>$ from a heat reservoir at $T_>$,

(2) gives an amount of heat $Q_<$ to another heat reservoir at $T_<$, and

(3) performs the mechanical work $\Delta W > 0$.

(c) The Carnot definition of temperature T and entropy S

Another definition of temperature is given via the so-called Carnot cycle. It is of physical conceptual use, since it involves explicitly the heat transfer, and hence the concept of state variables or non-state variables.

It is also of historical importance, since thermodynamic cycles played an essential role in the development of thermodynamics during the 19th century.

The Carnot cycle allows to transform undirected thermal motion (heat) into directed motion (mechanical work):

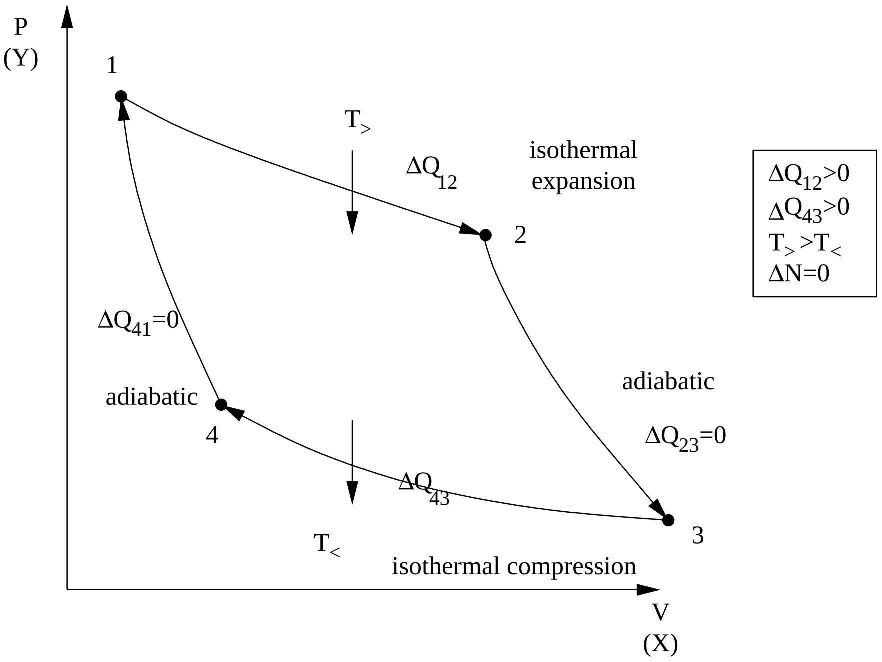

Figure 2.7: Carnot process

$1 \rightarrow 2:$	isothermal expansion	contact with heat bath 1
	$T = \text{const.} = T_>$	(slow)
$2 \rightarrow 3:$	adiabatic	no contact with heat bath
	$T \searrow \quad \Delta T = T_< - T_> < 0$	(fast)
$3 \rightarrow 4:$	isothermal compression	contact with heat bath 2
	$T = \text{const.} = T_<$	(slow)
$4 \rightarrow 1:$	adiabatic compression	no contact with heat bat*h*
	$T \nearrow \quad \Delta T = T_> - T_< > 0$	(fast)

Efficiency of the cycle:

$$\boxed{\eta = \frac{\text{mechanical work}}{\text{heat injected}} = \frac{\Delta W_{\text{tot}}}{\Delta Q_{12}}} \quad \text{per cycle} \tag{2.37}$$

(heat added *to system* is counted > 0, work done *by system* is counted < 0. Energy always counted wrt. the system, not reservoir.)

Since the internal energy is a state variable, its total change around a cycle must be zero:

$$\begin{aligned} 0 = \Delta U_{\text{tot}} &= \Delta Q_{\text{tot}} - \Delta W_{\text{tot}} & (2.38)\\ &= \Delta Q_{12} - \Delta Q_{43} - \Delta W_{\text{tot}} & (2.39)\\ \Delta W_{\text{tot}} &= \Delta Q_{12} - \Delta Q_{43} & (2.40) \end{aligned}$$

$$\boxed{\eta = 1 - \frac{\Delta Q_{43}}{\Delta Q_{12}} < 1} \quad \text{since}\, \Delta Q_{43} > 0 \tag{2.41}$$

The Carnot process is the most efficient heat engine.

Proof:
Assume that there is a heat engine A with $\eta_A > \eta$. Then, let engine A and Carnot engine C work between the same heat reservoir at $T_>$ and $T_<$. A can drive C as a cooling machine:

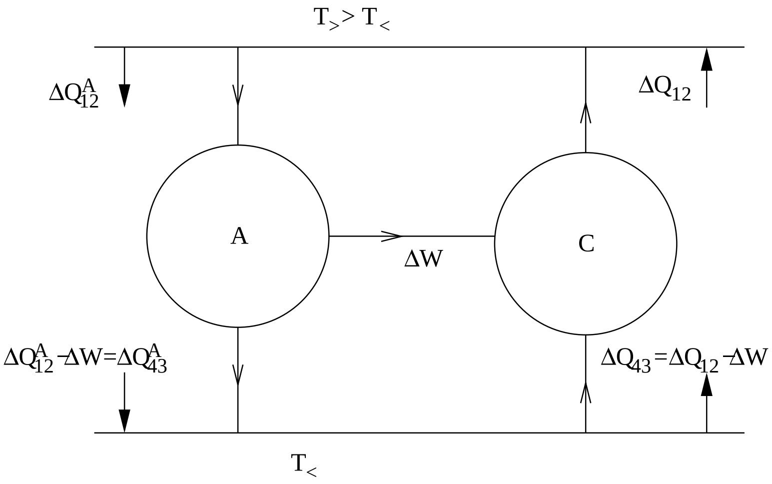

Figure 2.8: Coupled heat engines

Since $\eta_A > \eta$,

$$\frac{\Delta W}{\Delta Q^A_{12}} > \frac{\Delta W}{\Delta Q_{12}} \qquad \text{or} \qquad \Delta Q_{12} > \Delta Q^A_{12} \tag{2.42}$$

Total heat transfer from $T_<$ to $T_>$:

$$\begin{aligned}\Delta Q &= (\Delta Q_{12} - \Delta W) - (\Delta Q_{12}^A - \Delta W) && (2.43)\\ &= \Delta Q_{12} - \Delta Q_{12}^A > 0 && (2.44)\end{aligned}$$

Forbidden by 2nd law! ↯

Definition of temperature using the efficiency of the Carnot cycle:

It follows from the previous argument that all Carnot engines operating between the same heat reservoirs $T_>, T_<$ have the same efficiency η. Therefore, η does not depend on the state variables of the system involved in the cycle, but only on the temperatures of the resrvoirs $T_>, T_<$:

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = f(T_>, T_<) \tag{2.45}$$

Consider now two Carnot engines coupled to each other via heat transfer:

$$\begin{aligned}\frac{\Delta Q_{43}}{\Delta Q_{12}} &= \underbrace{f(T_>, T')}_{\text{same function } f} && (2.46)\\ \frac{\Delta Q_{65}}{\Delta Q_{43}} &= f(T', T_<) && (2.47)\\ \frac{\Delta Q_{65}}{\Delta Q_{12}} &= f(T_>, T_<) && (2.48)\end{aligned}$$

$\Rightarrow$ Functional equation for $f(T_>, T_<)$:

$$f(T_>, T_<) = f(T_>, T')\, f(T', T_<) \tag{2.49}$$

It has the solution

$$f(T_>, T_<) = \frac{g(T_>)}{g(T_<)} \tag{2.50}$$

with a universal function $g(T)$, which must be monotonically decreasing, since

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = \frac{g(T_>)}{g(T_<)} < 1 \quad \text{in order for } \eta > 0\ . \tag{2.51}$$

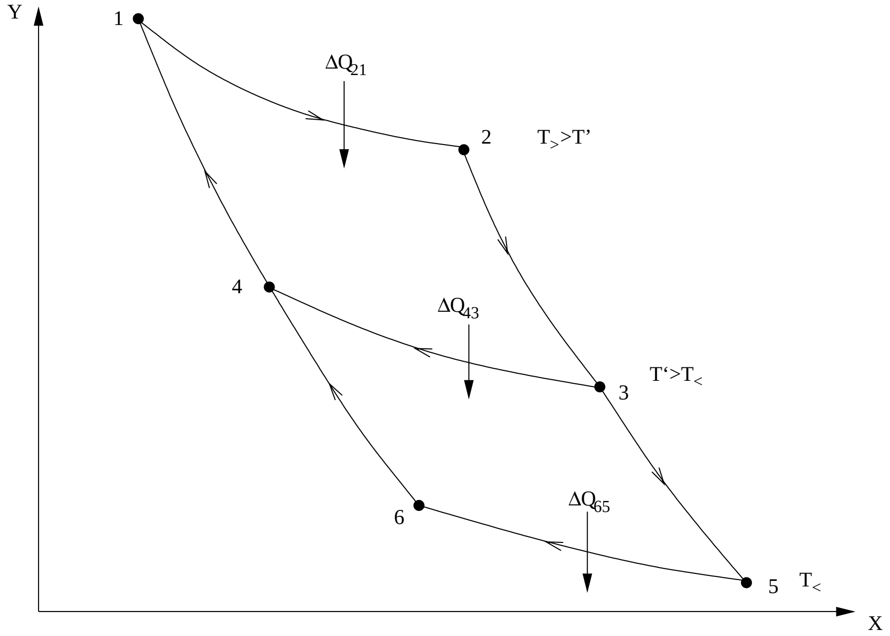

Figure 2.9: Two coupled Carnot processes

The Kelvin temperature scale is defined through the *choice*

$$g(T) = \frac{1}{T} \ . \tag{2.52}$$

Note the ambiguity in the definition. Hence,

$$\boxed{\eta = 1 - \frac{\Delta Q_{43}}{\Delta Q_{12}} = 1 - \frac{T_<}{T_>}} \tag{2.53}$$

It is shown within the microscopic kinetic gas theory that both definitions of the Kelvin scale are equivalent.

Definition of the state variable entropy

- For any Carnot cycle we have

$$\eta = 1 - \frac{\Delta Q_{43}}{\Delta Q_{12}} = 1 - \frac{T_<}{T_>} \tag{2.54}$$

and with $\Delta Q_{34} = -\Delta Q_{43} < 0$

$$\frac{\Delta Q_{12}}{T_>} + \frac{\Delta Q_{34}}{T_<} = 0 \ . \tag{2.55}$$

- Any arbitrary *reversible* (→ see discussion below) cyclic process can be decomposed into an infinite number of infinitesimal Carnot cycles.

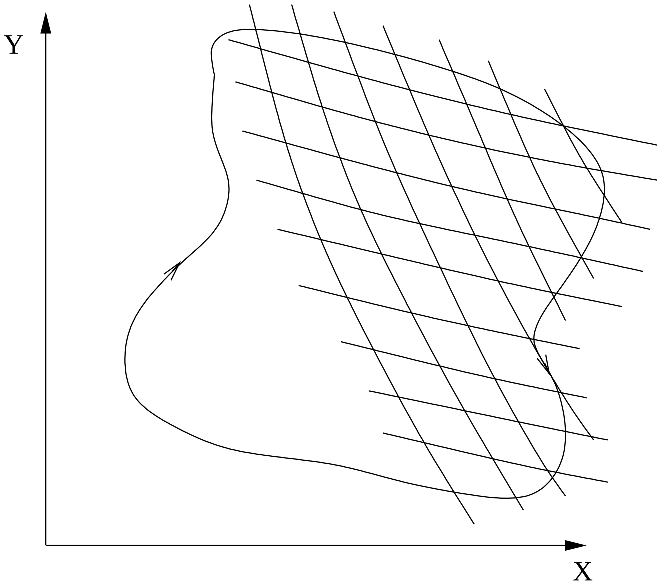

Figure 2.10: Any cyclic process can be decomposed into (infinitesimal) Carnot cycles

The amounts of heat exchanged between neighboring Carnot processes in the interior of the area compensate each other, so that only the contributions from the boundaries remain.
⇒ For a general *reversible* cycle:

$$\oint \frac{\delta Q}{T} = 0 \tag{2.56}$$

(Non-exact variations will be denoted by greek δQ.)

The quantity $dS = \frac{\delta Q}{T}$ is a complete differential of a state variable. The corresponding *state variable*

$$S = \int \frac{\delta Q}{T} \qquad \text{(for a reversible process)} \tag{2.57}$$

is called entropy. It will be related to the "disorder" in the system in statistical mechanics.

Remark:
For a *reversible* process the relation $dS = \frac{\delta Q}{T}$ holds and is an exact (= complete) differential, since it was derived for a collection of reversible Carnot cycles. For *irreversible* processes the relation

$$S = \int \frac{\delta Q}{T}\,, \quad dS = \frac{\delta Q}{T} \tag{2.58}$$

no longer holds, but the state variable S can still be defined. The relation $dS \leftrightarrow \delta Q$ will be discussed next.

The behavior of the entropy during thermodynamic changes of state: reversible and irreversible processes

All the process steps of the Carnot cycle are, by construction, performed in a time reversible way:

- The *isothermal* expansion ($1 \rightarrow 2$) and compression ($3 \rightarrow 4$) are done infinitely slowly, so that the working system is in equilibrium with the reservoir ($T_>$ and $T_<$, respectively) at each instant of time. *Such a process is always reversible.* This is because during each infinitesimal time interval between two *equilibrium* states only an *infinitesimal* amount of heat is transferred between system and reservoir. Therefore, each infinitesimal step is reversible. That the infinite series of infinitesimal steps is still reversible is at the heart of the postulate of the 2nd law and can be understood in a deeper way only from the microscopic concept of entropy as a measure for "disorder" in statistical mechanics. The problem will be re-visited there.
- The *adiabatic* expansion ($2 \rightarrow 3$) or compression ($4 \rightarrow 1$) are done without contact of the system with the reservoir (infinitely fast). Therefore, the internal (potential) energy of the system is completely transformed into mechanical work (since no other form of energy available), i.e. the adiabatic process is reversible.

In practice, however, the processes described above are not ideal:

1. No process can be done infinitely slowly. As a consequence, turbulences (or other disturbances) are generated in the gas (system), are ultimately transformed into additional indirected motion in the gas (i.e. heat) and lead to *irreversible* losses.

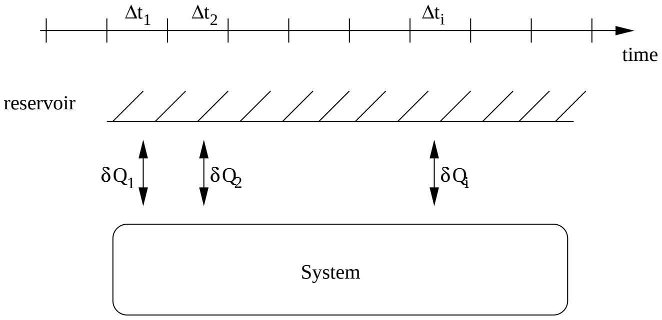

Figure 2.11: Reversible infinitesimal heat exchanges δQ_i

2. Turbulences with the same effect are also generated during the fast, adiabatic processes.
3. No system can be completely isolated from its surroundings, i.e. the adiabatic process itself is an idealization.
4. Frictional losses occur in real systems during each of the steps.

→ In an *irreversible* cyclic process less than the maximum possible fraction of the heat extracted from reservoir $T_>$ is transformed into mechanical work.
I.e. cyclic processes which include *irreversible* processes have a smaller efficiency than the Carnot cycle. Conversely, all *reversible* cyclic processes have the same maximum efficiency η.

Hence, we have

$$\eta_{irrev} = 1 + \frac{\overbrace{Q_{34}}^{=-Q_{43}}}{Q_{12}} \quad < \quad \eta = 1 - \frac{T_<}{T_>} \tag{2.59}$$

$$\text{or} \quad \frac{\Delta Q_{12}}{T_>} + \frac{\Delta Q_{34}}{T_<} \quad < \quad 0\,, \quad \text{and infinitesimally} \tag{2.60}$$

$$\oint \frac{\delta Q}{T} < 0 \tag{2.61}$$

for irreversible processes.

Note: T is an *equilibrium* concept and may not even be defined in an arbitrary irreversible process.

Or for state change $1 \rightarrow 2$:

$$\underbrace{\int_1^2 \frac{\delta Q}{T}}_{\text{irrev}} \leq \underbrace{\int_1^2 \frac{\delta Q}{T}}_{\text{rev}} \equiv \underbrace{\int_1^2 dS}_{\text{rev}} = \Delta S_{1\rightarrow 2} \tag{2.62}$$

$\Rightarrow$ In a thermally isolated system ($\delta Q \equiv 0$) the entropy S cannot decrease in any change of state $1 \rightarrow 2$:

$$\Delta S_{1\rightarrow 2} \geq 0 \qquad \text{thermally isolated systems} \tag{2.63}$$

This is a mathematical restatement of the 2nd law.

It follows an important, central conclusion of thermodynamics:
Since any system, left to itself (thermally isolated), reaches for time $t \rightarrow \infty$ the equilibrium state (= definition of equilibrium), and since this final state is reached through a succession of state changes with $\Delta S \geq 0$ each, the exact statement holds:

In thermodynamic equilibrium, for any set of values of the relevant state variables (N, V, $\vec{B}$, ...) which can be fixed *externally*, the entropy S of the system takes the maximum value as a function of the other variables, as illustrated in figure 12.

2.4.3 The third law of thermodynamics

The entropy of any closed (no heat, particle, ... exchange) thermodynamic system, which has a non-degenerate ground state, vanishes for $T \rightarrow 0$:

$$\boxed{\lim_{T\rightarrow 0} S(T) = 0} \tag{2.64}$$

The requirement ”non-degenerate ground state” is the essential condition for the 3rd law. Hence, it is a consequence of quantum mechanics, since in classical mechanics there are many degenerate minimum energy states possible for a many-particle system due to the classical distinguishability of particles. This problem

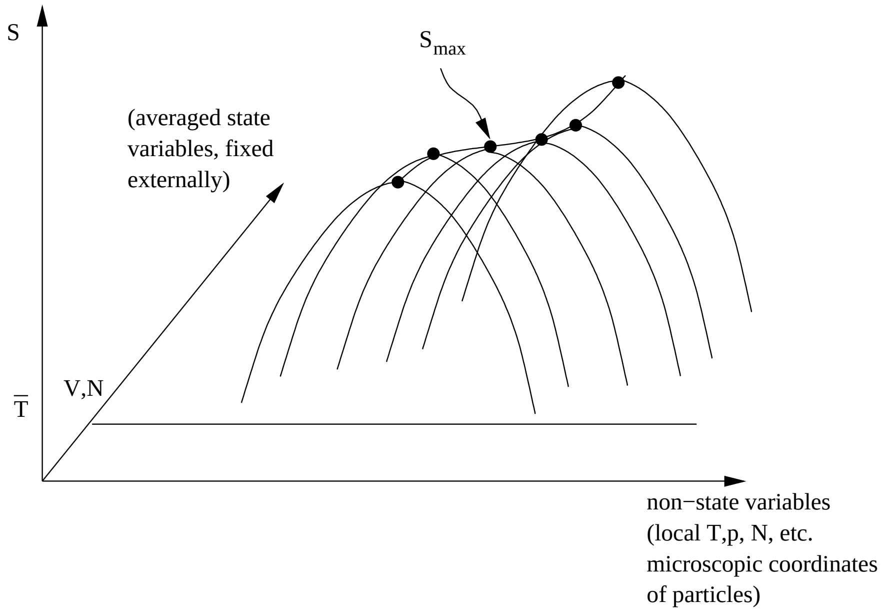

Figure 2.12: In equilibrium the entropy assumes a global maximum as a function of “non-state” variables.

is only lifted by the nondistinguishability of equivalent particles in quantum mechanics. Therefore, quantum mechanics has profound consequences even on the properties of macroscopic systems. This will be discussed further in statistical mechanics.

2.5 The fundamental relation of thermodynamics

The relation between the infinitesimal changes of the state variables manifested in the 1st law can be cast into a non-infinitesimal relation using a scaling argument: The 2nd law implies for *reversible* processes:

$$\delta Q = TdS \tag{2.65}$$

i.e. from the 1st law (energy conservation):

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN \tag{2.66}$$

(S is a homogenous function of an external variable.)
Hence, the derivatives of S wrt. U, V, N are

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} \tag{2.67}$$

$$\left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{T} \tag{2.68}$$

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T} \tag{2.69}$$

It follows from equation 2.66 that S is a function of the *extensive* variables U, V, N (which are proportional to the system size, "scale" with system size) in such a way that S scales with U, V, N, i.e. S is also proportional to the system size:

The entropy S is an extensive quantity.

Then the scaling relation holds,

$$(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N) \tag{2.70}$$

which implies by differentiation wrt. λ and $\lambda \to 1$,

$$\frac{d}{d\lambda}(\lambda S) = S = \frac{\partial S}{\partial U}U + \frac{\partial S}{\partial V}V + \frac{\partial S}{\partial N}N \tag{2.71}$$

and using $\frac{\partial S}{\partial U}$, $\frac{\partial S}{\partial V}$, $\frac{\partial S}{\partial N}$ above,

$$TS = U + PV - \mu N \tag{2.72}$$

$$\boxed{\Leftrightarrow\ U = TS - PV + \mu N\ .} \qquad \text{Fundamental relation of thermodynamics} \tag{2.73}$$

S is a homogenous function of U, V, N.

It can be seen as a non-infinitesimal form of the 1st law, where now *both* the extensive variables S, V, N and the intensive variables T, P, μ can be varied (by changing e.g. external parameters). The *total* differential of the fundamental relation implies another relation between thermodynamic derivatives:

$$TdS + SdT = dU + PdV + VdP - \mu dN - Nd\mu \tag{2.74}$$

and with the 1st law

$$dU = TdS - PdV + \mu dN : \tag{2.75}$$

$$\boxed{d\mu = -\frac{S}{N}dT + \frac{V}{N}dP} \qquad \text{Gibbs-Duhem-relation} \tag{2.76}$$

Using particle density $\rho = \frac{N}{V}$ and entropy density $s = \frac{S}{V}$ one obatins:

$$\boxed{d\mu = -\frac{1}{\rho}sdT + \frac{1}{\rho}dP} \tag{2.77}$$

The fundamental relation can be used to derive the equations of state for specific state changes from the general equation of state, $F(P, V, T, \ldots) = 0$.
Equation for an ideal gas:

$$\begin{aligned} F(P,V,T) &= PV - Nk_BT = 0 \quad \text{general EOS} && (2.78)\\ \underbrace{\Rightarrow}_{F.R.} F_{\delta Q=0}(P,V,T) &= 0 \quad \text{adiabatic equation} && (2.79)\\ F_{dT=0}(P,V,T) &= 0 \quad \text{isothermal equation, etc.} && (2.80) \end{aligned}$$

2.6 Thermodynamic potentials

The internal energy U of a system describes (but is not equivalent to, since $\eta < 1$) the energy stored in the system, i.e. potential energy, that can be transformed into mechanical work. It is, therefore, often called a *thermodynamical potential.*

Example:

$$\Delta U = \Delta Q - \Delta W \tag{2.81}$$

work done by the gas:

$$\begin{aligned} \Delta W &= -(\Delta U - \Delta Q) > 0 && (2.82)\\ |\Delta W| &< \Delta U && (2.83) \end{aligned}$$

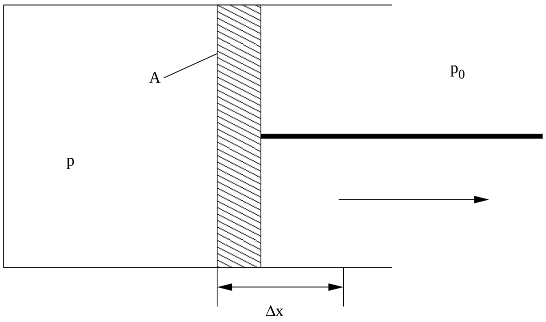

Figure 2.13: Mechanical work ΔW done against external pressure P_0

The 2nd law implies a *minimum principle for* U:
For reversible and irreversible processes $1 \to 2$ we have

$$\begin{aligned} \delta Q &= T dS \quad \text{for reversible processes} && (2.84)\\ \delta Q &< T dS \quad \text{for irreversible processes} && (2.85)\\ \Delta U &\le \underbrace{\int_1^2 T\, dS}_{\Delta Q} - \Delta W_{12} + \int_1^2 \mu\, dN && (2.86) \end{aligned}$$

i.e. in a *closed* system with S, V, $N =$ const. and S a fixed variable in U (→ see below):

$$\boxed{(\Delta U)_{S,V,N} \le 0} \quad \text{for any processes in a closed system.} \tag{2.87}$$

The internal energy U has been written as a function of all the extensive variables of the system, S, V, N, ...
U is, therefore, useful to describe processes where S, V, N, ... are *fixed* from outside, i.e. the minimum of U as function of S, V, N (dS, dV, $dN = 0$) is determined for given S, V, N, and hence the corresponding T, P, μ, ...
→ exercises
→ examples (below)
In many cases, S, V, N (especially S) are not determined from outside. It is then useful to write the "potential energy" of the system as function of the relevant, externally determined variables, i.e. of intensive or extensive variables, or a combination. For each *extensive* variable there is an *intensive* quantity

which is the derivative of U wrt. the extensive one; both variables form a pair of canonically conjugated variables:

$$S \quad \rightarrow \quad T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \tag{2.88}$$

$$V \quad \rightarrow \quad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \tag{2.89}$$

$$N \quad \rightarrow \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \qquad \text{etc.} \tag{2.90}$$

We want to write U not as a function of S but as function of T, the derivative of U wrt. S.

The standard way to write a given function $f(y)$ *locally* in dependence of $\Pi = \frac{\partial f}{\partial y}$ is the Legendre transformation.

$$f(y): \qquad f = \Pi dy \tag{2.91}$$

$$g(\Pi) = f - \Pi y: \qquad dg = \underbrace{df - \Pi dy}_{=0} - yd\Pi = -yd\Pi \tag{2.92}$$

Recipe: $f \rightarrow g$: subtract pair of conjugated variables.

Example: Classical mechanics
Transformation from Lagrange function $L(x, \underbrace{\dot{x}}_{y})$ to Hamilton function $H(x, p)$, where the coordinate x is an unchanged variable, the velocity $\dot{x}$ corresponds to y, and the classical momentum $p = \frac{\partial L}{\partial \dot{x}}$ corresponds to Π:

$$H = L - x\frac{\partial L}{\partial \dot{x}} \tag{2.93}$$

Note:

- It is only necessary to perform a *local* transformation in the vicinity of some given value of the variable y, since we are looking for the minimum of f.
- *Locally*, the Legendre transformation is unique.
- If $f(y)$ has a minimum (extremum) at a given point y then $g(\Pi)$ has a minimum (extremum) at the same point, (only expressed by the variable Π), and vice versa.

Application to thermodynamics:

external fixed variables	thermodynamic potential
S, P, N	enthalpy $H(S,P,N) = U + PV = ST + \mu N$ $dH = TdS + VdP + \mu dN$
T, V, N	free energy (Helmholtz free energy) $F(T,V,N) = U - TS = -PV + \mu N$ $dF = -SdT + PdV + \mu dN$
T, P, N	free energy (Gibbs free energy) $G(T,P,N) = U - TS + PV = \mu N$ $dG = -SdT + VdP + \mu dN$
T, V, μ	grand canonical potential $\Omega(T,V,\mu) = U - TS - \mu N = -PV$ $d\Omega = -SdT - PdV - Nd\mu$ (for systems with particle exchange)
S, V, N	$U(S,V,N) = TS - PV + \mu N$ $dU = TdS - pdV + \mu dN$

Relations between thermodynamic derivatives: Maxwell relations

From $dU = TdS - pdV + \mu dN$ it follows:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \tag{2.94}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \tag{2.95}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{2.96}$$

Taking another derivative and using $\frac{\partial^2 U}{\partial x \partial y} = \frac{\partial^2 U}{\partial y \partial x}$ for state variables, one obtains immediately

$$\boxed{\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_{S,N} &= -\left(\frac{\partial P}{\partial S}\right)_{V,N} \\ \left(\frac{\partial T}{\partial N}\right)_{S,V} &= \left(\frac{\partial \mu}{\partial S}\right)_{V,N} \\ \left(\frac{\partial P}{\partial N}\right)_{S,V} &= -\left(\frac{\partial \mu}{\partial V}\right)_{S,N} \end{aligned}} \quad \text{Maxwell relations} \tag{2.97}$$

and similar relations for other variables.

2.7 Thermodynamic response functions

The response of a thermodynamic system to the change of external parameters, like temperature T, magnetic field $\vec{B}$, pressure p, etc., is described by the response functions. If these external functions are time-independent, the response functions can be expressed as derivatives of the thermodynamic potentials.

2.7.1 Thermal response functions

The thermal response functions or *specific heats c* describe the change of the heat content δQ of a system (per volume) due to a change of temperature T in a reversible process:

$$c = \frac{\delta Q}{\mathrm{d}T} = T\frac{\mathrm{d}S}{\mathrm{d}T} \tag{2.98}$$

where it must be specified, which other variables are kept constant during that process.

For the $N-p-V$ system, the particle number N and either V or p are kept constant. Hence, one has

$$\begin{aligned}
c_V &= T\left(\frac{\partial S}{\partial T}\right)_{V,N} && (2.99)\\
&\uparrow && (2.100)\\
\mathrm{d}F &= S\mathrm{d}T - p\underbrace{\mathrm{d}V}_{=0} + \mu\underbrace{\mathrm{d}N}_{=0} && (2.101)\\
&= -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} && (2.102)\\
&> 0 && (2.103)
\end{aligned}$$

or equivalently, since $\mathrm{d}U = \delta Q - p\mathrm{d}V + \mu\mathrm{d}N$,

$$c_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} \tag{2.104}$$

$$\begin{aligned}
c_p &= T\left(\frac{\partial S}{\partial T}\right)_{p,N} && (2.105)\\
&\uparrow && (2.106)\\
\mathrm{d}G &= S\mathrm{d}T - V\underbrace{\mathrm{d}p}_{=0} + \mu\underbrace{\mathrm{d}N}_{=0} && (2.107)\\
&= -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N} && (2.108)\\
&> 0 && (2.109)
\end{aligned}$$

or equivalently, with $\mathrm{d}H = \delta Q - V\mathrm{d}p + \mu\mathrm{d}N$,

$$c_p = \left(\frac{\partial H}{\partial T}\right)_{p,N} \tag{2.110}$$

It follows from the second law of thermodynamics (formulation (2)) that the specific heat is positive:

$$c_V > 0, \qquad c_p > 0 \tag{2.111}$$

2.7.2 Mechanical response functions

The *compressibility* κ describes the change of volume of a system due to a pressure change, normalized to its volume:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial p^2}\right)_{T,N} \geq 0 \tag{2.112}$$

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{S,N} = -\frac{1}{V}\left(\frac{\partial^2 H}{\partial p^2}\right)_{S,N} \geq 0 \tag{2.113}$$

The stability of a physical system requires that the compressibility is not negative (no spontaneous volume collapse).

The compressibility can also be expressed in terms of the density $n = \frac{N}{V}$:

$$\frac{1}{n}\left(\frac{\partial n}{\partial p}\right)_N = \frac{V}{N}\left(-\frac{N}{V^2}\right)\frac{\partial V}{\partial p} = \kappa \tag{2.114}$$

The change of volume due to a temperature change is given by the *thermal expansion coefficient* α

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left\{\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)_T\right\} \gtrless 0 \tag{2.115}$$

The heat expansion α can be positive or negative.

2.7.3 Magnetic response functions

The magnetic susceptibility $\chi_{T,S}$ is the response of the magnetization M to a change of the external magnetic field B:

$$\begin{array}{rcl} \chi_T = \left(\dfrac{\partial M}{\partial B}\right)_T & = & \left(\dfrac{\partial^2 F_{T,B}}{\partial B^2}\right)_T \qquad (2.116) \\ & \uparrow & \\ & \mathrm{d}F_{T,B} & = -S\mathrm{d}T - p\mathrm{d}V + M\mathrm{d}B \\ \chi_S = \left(\dfrac{\partial M}{\partial B}\right)_S & = & \left(\dfrac{\partial^2 F_{S,B}}{\partial B^2}\right)_S \qquad (2.117) \\ & \uparrow & \\ & \mathrm{d}F_{S,B} & = S\mathrm{d}T - p\mathrm{d}V + M\mathrm{d}B \end{array}$$

where the “free energies” of a magnetic system, $F_{T,B}, F_{S,B}$ are understood as the Legendre transforms of U with respect to T and B and to S and B, respectively.

The susceptibility is positive for a para- or ferromagnetic system and negative for a diamagnetic system.

The relations given in 1.6.1-1.6.3 show generally, that the response functions can be expressed in terms of the second derivatives of an appropriate thermodynamic potential.

2.7.4 Relations between thermal and mechanical response functions

The following relations hold:

$$\frac{c_p}{c_V} = \frac{\kappa_T}{\kappa_S} \tag{2.118}$$

$$c_p - c_V = TV\frac{\alpha_p^2}{\kappa_T} \geq 0 \tag{2.119}$$

Proof:

- *Relation (1)*:

$$\frac{c_p}{c_V} = \frac{\left(\frac{\partial S}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_V} = \frac{\frac{(\partial p/\partial T)_S}{(\partial p/\partial S)_T}}{\frac{(\partial V/\partial T)_S}{(\partial V/\partial S)_T}} = \frac{\frac{(\partial V/\partial S)}{\partial p/\partial S}\Big|_T}{\frac{(\partial V/\partial T)}{(\partial p/\partial T)}\Big|_S} = \frac{\left(\frac{\partial V}{\partial p}\right)_T}{\left(\frac{\partial V}{\partial p}\right)_S} = \frac{\kappa_T}{\kappa_S} \tag{2.120}$$

where we used in the numerator, that the *total* differential of p vanishes for c_p:

$$0 = \mathrm{d}p = \left(\frac{\partial p}{\partial S}\right)_T \mathrm{d}S + \left(\frac{\partial p}{\partial T}\right)_S \mathrm{d}T \Rightarrow \left(\frac{\partial S}{\partial T}\right)_p = -\frac{\left(\frac{\partial p}{\partial T}\right)_S}{\left(\frac{\partial p}{\partial S}\right)_T} \tag{2.121}$$

and in the denominator, that the total differential of V vanishes for c_V:

$$0 = \mathrm{d}V = \left(\frac{\partial V}{\partial S}\right)_T \mathrm{d}S + \left(\frac{\partial V}{\partial T}\right)_S \mathrm{d}T \Rightarrow \left(\frac{\partial S}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_S}{\left(\frac{\partial V}{\partial S}\right)_T} \tag{2.122}$$

- *Relation (2)*:

$$c_p - c_V = T\left\{\left(\frac{\partial S}{\partial T}\right)_p - \left(\frac{\partial S}{\partial T}\right)_V\right\} \tag{2.123}$$

(i) We use the chain rule to express the T-derivative at $p =$ const. by a T-derivative at $V =$ const. (see also above):

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{\partial}{\partial T} S(T, V(p,T))\Big|_{p=\text{const.}} \tag{2.124}$$

$$= \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \underbrace{\left(\frac{\partial V}{\partial T}\right)_p}_{V\cdot\alpha_p} \tag{2.125}$$

(ii) $\left(\frac{\partial S}{\partial V}\right)_T$ is expressed using a Maxwell relation, employing the thermodynamical potential F:

$$
\begin{aligned}
S &= -\left(\frac{\partial F}{\partial T}\right)_V && (2.126)\\
\left(\frac{\partial S}{\partial V}\right)_T &= -\left\{\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V\right\}_T = \left\{\frac{\partial}{\partial T}\left(-\frac{\partial F}{\partial V}\right)_T\right\}_V && (2.127)\\
&= \left(\frac{\partial p}{\partial T}\right)_V && (2.128)
\end{aligned}
$$

Since in the last expression $\mathrm{d}V = 0$, we have

$$
\begin{aligned}
0 &= \mathrm{d}V = \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T && (2.129)\\
\Rightarrow \quad \left(\frac{\partial p}{\partial T}\right)_V &= -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} = -\frac{V\alpha_p}{(-V\kappa_T)} = \frac{\alpha_p}{\kappa_T} && (2.130)
\end{aligned}
$$

and finally

$$
c_p - c_V = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p = TV\frac{\alpha_p^2}{\kappa_T} \geq 0. \qquad (2.131)
$$

Physically $c_p \geq c_V$, because for $p =$ const. part of the heat added is not kept in the system but is transformed to mechanical work. Thus, more heat is necessary to make a given temperature change than in the case $V =$ const.

Similarly, one can prove the magnetic relations:

$$
\boxed{
\begin{aligned}
\frac{c_B}{c_M} &= \frac{\chi_T}{\chi_S}\\
c_B - c_M &= T\frac{\alpha_B^2}{\chi_T} \geq 0
\end{aligned}
} \qquad (2.132)
$$