Introduction

- Thermodynamics: phenomenological description of equilibrium bulk properties of matter in terms of only a few "state variables" and thermodynamical laws.

- *Statistical physics:* microscopic foundation of thermodynamics

- $\sim 10^{23}$ degrees of freedom $\rightarrow$ 2–3 state variables!

- "Everything should be made as simple as possible, but no simpler" (A. Einstein)

Summary of contents:

- Review of thermodynamics

- Thermodynamical potentials

- Phase space and probability

- Quantum mechanical ensembles

- Equilibrium ensembles

- Ideal fluids

- Bosonic systems

- Fermionic systems

- Interacting systems

- Phase transitions and critical phenomena

1. Foundations of thermodynamics

1.1. Fundamental thermodynamical concepts

System : macroscopic entity under consideration.

Environment : world outside of the system (infinite).

Open system : can exchange matter and heat with the environment.

Closed system : can exchange heat with the environment while keeping the number of particles fixed.

Isolated system : can exchange neither matter nor heat with the environment. Can (possibly) still do work by e.g. expanding.

Thermodynamical equilibrium:

- No macroscopic changes.

- Uniquely described by (a few) external variables of state.

- System forgets its past: no memory effects, no hysteresis.

- Often the term *global equilibrium* is used, as opposed to local equilibrium, which is not full equilibrium at all (next page)!

Nonequilibrium:

- Generally much more complicated than equilibrium state.

- Simplest case: isolated systems each in an equilibrium state.

- In a *local thermodynamical equilibrium* small regions are locally in equilibrium, but neighbour regions in different equilibria $\Rightarrow$ particles, heat etc. will flow. Example: fluid (water) with non-homogeneous temperature.

- Stronger nonequilibrium systems usually *relax* to a local equilibrium.

Degrees of freedom (d.o.f.) is the number of quantities needed for the exact description of the microscopic state.

Example: classical ideal gas with N particles: $3N$ coordinates (x, y, z), $3N$ momenta (p_x, p_y, p_z).

State variables are parameters characterizing the macroscopic thermodynamical state. These are all *extensive* or *intensive*:

Extensive variable: change value when the size (spatial volume and the number of degrees of freedom) is changed: volume V, particle number N, internal energy U, entropy S, total magnetic moment $\int d^3r \, \boldsymbol{M}$.

Intensive variable: independent of the size of the system, and can be determined for every semimicroscopical volume element: e.g. temperature T, pressure p, chemical potential μ, magnetic field $\boldsymbol{H}$, ratios of extensive variables like $\rho = N/V$, $s = S/N, \ldots$.

Conjugated variables: A and B appear in pairs in expressions for the differential of the energy (or more generally, some state variable), i.e. in forms $\pm A\,dB$ or $\pm B\,dA$; one is always extensive and the other intensive.

Example: pressure p and volume V; change in internal energy U when V is changed (adiabatically, at constant S) is $dU = -pdV$.

Process is a change in the state.

Reversible process: advances via states infinitesimally close to equilibrium, *quasistatically* ("slow process"). The direction of a reversible process can be reversed, obtaining the initial state (for system + environment!)

Isothermal process : T constant.

Isobaric process : p constant.

Isochoric process : V constant.

Isentropic or **adiabatic process**: S constant.

Irreversible process is a sudden or spontaneous change during which the system is far from equilibrium. In the intermediate steps global state variables (p, T, ...) are usually not well defined.

Cyclic process consists of cycles which take the system every time to its initial state.

1.2. State variables and exact differentials

Let us suppose that, for example, the state of the system can be uniquely described by state variables T, V ja N. Other state variables are then their unique functions:
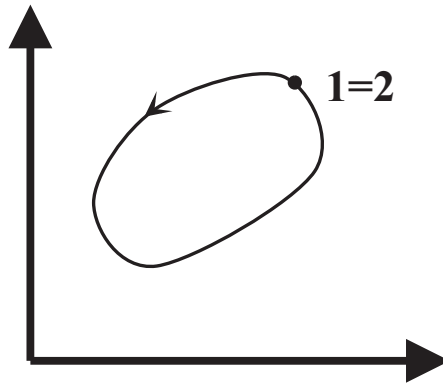
$$
\begin{aligned}
p &= p(T, V, N) \\
U &= U(T, V, N) \\
S &= S(T, V, N) \dots
\end{aligned}
$$

By applying differential calculus, the differential of p, for example, is

$$
dp = \left(\frac{\partial p}{\partial T}\right)_{V,N} dT + \left(\frac{\partial p}{\partial V}\right)_{T,N} dV + \left(\frac{\partial p}{\partial N}\right)_{T,V} dN
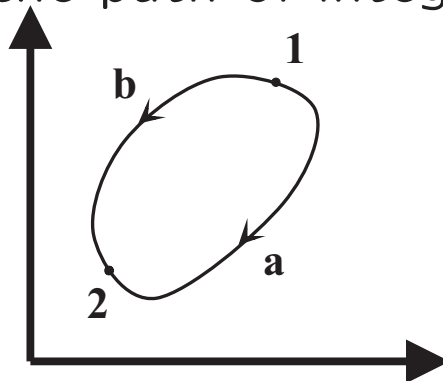$$

$\vdots$

The differentials of state variables, dp, dT, dV, ..., are **exact differentials**. These have the following properties

(A) Their total change evaluated over a closed path vanishes:

$$\oint_{1\to 2} dp = \oint_{1\to 2} dU = \cdots = 0.$$

(B) The total change of an exact differential is independent on the path of integration:

$$\int_a dU - \int_b dU = 0,$$

so that we can write

$$U(2) = U(1) + \int_1^2 dU$$

Exact differentials

Let us denote by $đF$ a differential which is not necessarily exact (i.e. integrals can depend on the path). Assuming it depends on 2 variables x, y, the differential

$$đF = F_1(x, y)\, dx + F_2(x, y)\, dy$$

is **exact differential** if

$$\frac{\partial F_1}{\partial y} = \frac{\partial F_2}{\partial x}.$$

Then $\exists F(x, y)$ so that $F_1(x, y) = \frac{\partial F(x, y)}{\partial x}$ and $F_2(x, y) = \frac{\partial F(x, y)}{\partial y}$ and

$$\int_1^2 đF = F(2) - F(1)$$

is independent on the path, and integrable. In this case (x, F_1) and (y, F_2) are pairs of conjugated variables with respect to F.

Examples: are the following differentials exact?

$$đF = y\, dx + x\, dy$$

$$đF = x\, dx + x\, dy$$

All physical state variables are exact differentials! This will enable us to derive various identities between state variables.

Integrating factor

If $đF = F_1 dx + F_2 dy$ is not exact, there exists an *integrating factor* $\lambda(x, y)$ so that in the neighbourhood of the point (x, y)

$$\lambda đF = \lambda F_1 dx + \lambda F_2 dy = df$$

is an exact differential. λ and f are state variables.

Example: find λ for the differential

$$đF = x\, dx + x\, dy \,.$$

Legendre transformations

Legendre transformations can be used to make changes in the set of the indepependent state variables. For example, let us look at the function $f(x, y)$ of two variables. We denote

$$z = f_y = \frac{\partial f(x, y)}{\partial y}$$

and define the function

$$g = f - y f_y = f - yz.$$

(Note: z, y is a congjugated pair with respect to f!) Now

$$
\begin{aligned}
dg &= df - y\, dz - z\, dy = f_x dx + f_y dy - y\, dz - z\, dy \\
&= f_x dx - y\, dz.
\end{aligned}
$$

Thus we can take x and z as independent variables of the function g, i.e. $g = g(x, z)$. Obviously

$$y = -\frac{\partial g(x, z)}{\partial z}.$$

Corresponding to the Legendre transformation $f \to g$ there is the inverse transformation $g \to f$

$$f = g - z g_z = g + yz.$$

Often needed identities

Let $F = F(x, y)$, $x = x(y, z)$, $y = y(x, z)$ and $z = z(x, y)$. If we want to give F in terms of (x, z), we can write

$$F(x, y) = F(x, y(x, z)).$$

Applying differential rules we obtain identities

$$\left(\frac{\partial F}{\partial x}\right)_z = \left(\frac{\partial F}{\partial x}\right)_y + \left(\frac{\partial F}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

$$\left(\frac{\partial F}{\partial z}\right)_x = \left(\frac{\partial F}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x$$

One can show that

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

and

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{\left(\frac{\partial F}{\partial y}\right)_z}{\left(\frac{\partial F}{\partial x}\right)_z}.$$

1.3. Equations of state

Encodes (some of the) physical properties of the equilibrium system. Usually these relate "mechanical" readily observable variables, like p, T, N, V; not "internal" variables like S, internal energy U etc. A typical example: pressure of some gas as a function of T and density ρ.

Some examples:

Classical ideal gas

$$\boxed{pV = Nk_BT}$$

where N = number of molecules
T = absolute temperature
$k_B = 1.3807 \cdot 10^{-23}$ J/K = Boltzmann constant.
Chemists use often the form

$$
\begin{aligned}
pV &= nRT \\
n &= N/N_0 = \text{number of moles} \\
R &= k_B N_0 = 8.315 \text{J/K mol} \\
&= \text{gas constant} \\
N_0 &= 6.0221 \cdot 10^{23} = \text{Avogadro's number.}
\end{aligned}
$$

If the gas is composed of m different species of molecules the equation of state is still

$$pV = Nk_BT,$$

where now

$$N = \sum_{i=1}^{m} N_i$$

and

$$p = \sum_i p_i, \qquad p_i = N_i k_B T / V,$$

where p_i is the partial pressure of the i:th component

Virial expansion of real gases

When the interactions between gas molecules are taken into account, the ideal gas law receives corrections which are suppressed by powers of density $\rho = N/V$:

$$\boxed{p = k_B T \left[\rho + \rho^2 B_2(T) + \rho^3 B_3(T) + \cdots\right]}$$

Here B_n is the n:th *virial coefficient*.

Van der Waals equation

The molecules of real gases interact

- repulsively at short distances; every particle needs at least the volume b $\Rightarrow$ $V \gtrsim Nb$.

- attractively (potential $\sim (r/r_0)^6$) at large distances due to the induced dipole momenta. The pressure decreases when two particles are separated by the attraction distance. The probability of this is $\propto (N/V)^2$.

We improve the ideal gas state equation

$$p'V' = Nk_BT$$

so that

$$
\begin{aligned}
V' &= V - Nb \\
p &= p' - a\rho^2 = \text{true pressure.}
\end{aligned}
$$

then

$$(p + a\rho^2)(V - Nb) = Nk_BT.$$

Solid substances

The thermal expansion coefficient

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N}$$

and the isothermal *compressibility*

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N}$$

of solid materials are very small, so the Taylor series

$$V = V_0(1 + \alpha_p T - \kappa_T p)$$

is a good approximation.

Typically

$$
\begin{aligned}
\kappa_T &\approx 10^{-10}/\text{Pa} \\
\alpha_p &\approx 10^{-4}/\text{K}.
\end{aligned}
$$

Stretched wire

Tension $[N/m^2]$

$$\sigma = E(T)(L - L_0)/L_0,$$

where L_0 is the length of the wire when $\sigma = 0$ and $E(T)$ is the temperature dependent elasticity coefficient.

Surface tension

$$
\begin{aligned}
\sigma &= \sigma_0 \left(1 - \frac{t}{t'}\right)^n \\
t &= \text{temperature } °C \\
t' \text{ and } n &\quad \text{experimental constants,} \\
&\quad 1 \lesssim n \lesssim 2 \\
\sigma_0 &= \text{surface tension when } t = 0°C.
\end{aligned}
$$

Electric polarization

When a piece of material is in an external electric field $\boldsymbol{E}$, we define

$$\boldsymbol{D} = \epsilon_0 \boldsymbol{E} + \boldsymbol{P},$$

where

$$
\begin{aligned}
\boldsymbol{P} &= \text{electric polarization} \\
&= \text{atomic total dipole momentum/volume} \\
\boldsymbol{D} &= \text{electric flux density} \\
\epsilon_0 &= 8.8542 \cdot 10^{-12} \text{As/Vm} \\
&= \text{vacuum permeability.}
\end{aligned}
$$

In homogenous dielectric material one has

$$\boldsymbol{P} = \left(a + \frac{b}{T} \right) \boldsymbol{E},$$

where a and b are almost constant and $a, b \geq 0$.

Curie's law

When a piece of paramagnetic material is in magnetic field $\boldsymbol{H}$ we write

$$\boldsymbol{B} = \mu_0(\boldsymbol{H} + \boldsymbol{M}),$$

where

$$
\begin{aligned}
\boldsymbol{M} &= \text{magnetic polarization} \\
&= \text{atomic total magnetic moment/volume} \\
\boldsymbol{B} &= \text{magnetic flux density} \\
\mu_0 &= 4\pi \cdot 10^{-7} \text{Vs/Am} = \text{vacuum permeability.}
\end{aligned}
$$

Polarization obeys roughly *Curie's* law

$$\boldsymbol{M} = \frac{\rho C}{T}\boldsymbol{H},$$

where ρ is the number density of paramagnetic atoms and C an experimental constant related to the individual atom.

Note Use as a thermometer: measure the quantity M/H.

1.4. 0th law of thermodynamics

If each of two bodies is separately in thermal equilibrium with a third body then they are also in thermal equilibrium with each other $\Rightarrow$ there exists a property called *temperature* and *thermometer* which can be used to measure it.

1.5. Work

Work is exchange of such "noble" energy (as opposed to exchange of heat or matter) that can be completely transformed to some other noble form of energy; e.g. mechanical and electromagnetic energy.

Sign convention: work ΔW is *the work done by the system to its environment.*

Example pVT system

$$\Delta W = p\,\Delta V.$$

Note $đW$ is *not* an exact differential: the work done by the system is not a function of the final state of the system (need to know the history!). Instead

$$\frac{1}{p}đW = dV$$

is exact, i.e, $1/p$ is the integrating factor for work.

Example

$$đW = p\,dV - \sigma A\,dL - \boldsymbol{E}\cdot d\boldsymbol{P} - \boldsymbol{H}\cdot d\boldsymbol{M}.$$

In general

$$đW = \sum_i f_i dX_i = \boldsymbol{f}\cdot d\boldsymbol{X},$$

where f_i is a component of a *generalized force* and X_i a component of a *generalized displacement*.

1.6. 1st law of thermodynamics

Total energy is conserved

In addition to work a system can exchange *heat (thermal energy)* or *chemical energy*, associated with the exchange of matter, with its environment. Thermal energy is related to the energy of the thermal stochastic motion of microscopic particles.

The total energy of a system is called **internal energy**.

Sign conventions:
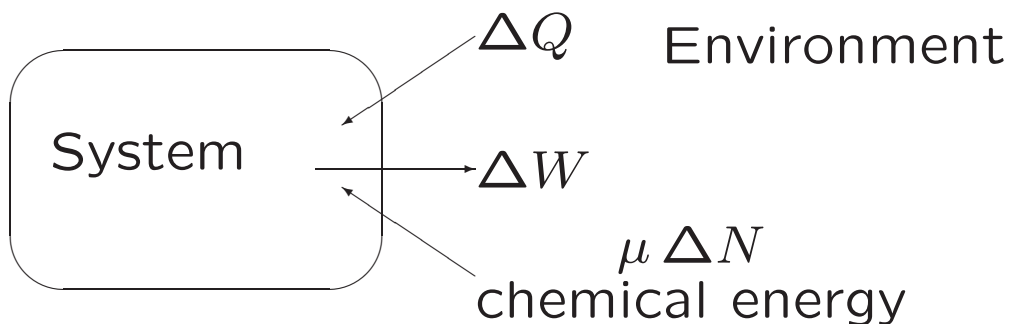
If the system can exchange heat and particles and do work, the energy conservation law gives the change of the internal energy

$$dU = đQ - đW + \mu dN,$$

where μ is the chemical potential. More generally,

$$dU = đQ - \boldsymbol{f} \cdot d\boldsymbol{X} + \sum_i \mu_i dN_i.$$

U is a state variable, i.e. dU is exact.

Cyclic process

In a cyclic process the system returns to the original state. Now $\oint dU = 0$, so $\Delta W = \Delta Q$ (no change in thermal energy). In a pVT-system
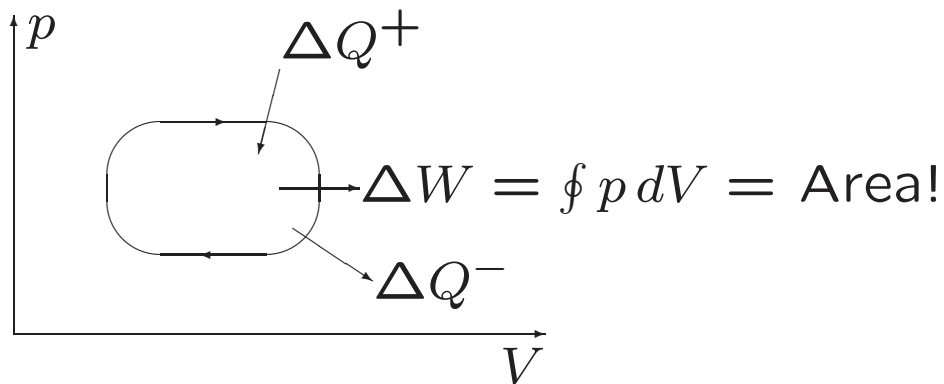
The total change of heat is

$$\Delta Q = \Delta Q^+ + \Delta Q^-,$$

where ΔQ^+ is the heat taken by the system and $-\Delta Q^-$ (> 0) the heat released by the system.

The *efficiency* η is

$$\eta = \frac{\Delta W}{\Delta Q^+} = \frac{\Delta Q^+ + \Delta Q^-}{\Delta Q^+} = 1 - \frac{|\Delta Q^-|}{|\Delta Q^+|}.$$

1.7. 2nd law of thermodynamics

Heat flows from high temperatures to low temperatures.

(a) Heat cannot be transferred from a cooler heat reservoir to a warmer one without other changes.

(b) In a cyclic process it is not possible to convert all heat taken from the hotter heat reservoir into work.

(c) It is not possible to reverse the evolution of a system towards thermodynamical equilibrium without converting work to heat.

(d) The change of the total entropy of the system and its environment is positive and can be zero only in reversible processes.

(e) Of all the engines working between the temperatures T_1 and T_2 the Carnot engine has the highest efficiency.

We consider the infinitesimal process
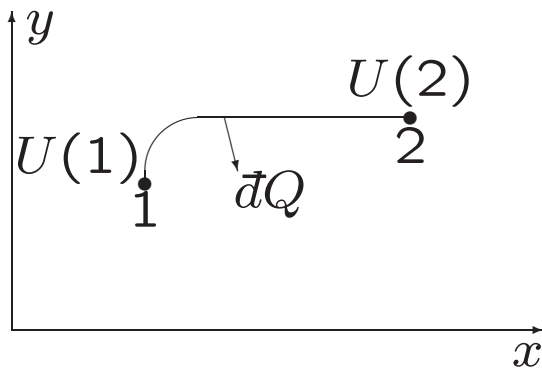
Now

$$\bar{d}Q = dU + \bar{d}W = dU + \boldsymbol{f} \cdot d\boldsymbol{X},$$

so there exists an integrating factor $1/T$ so that

$$\frac{1}{T}\bar{d}Q = dS$$

is exact. The state variable S is *entropy* and T turns out to be *temperature* (on an absolute scale)

The second law (d) can now be written as

$$\frac{dS_{\text{tot}}}{dt} \geq 0,$$

where S_{tot} is the entropy of the system + environment.

For the entropy of the system only we have

$$dS \geq \frac{1}{T}\,\bar{d}Q,$$

where the equality holds only for reversible processes. The entropy of the system can decrease, but the total entropy always increases (or stays constant).

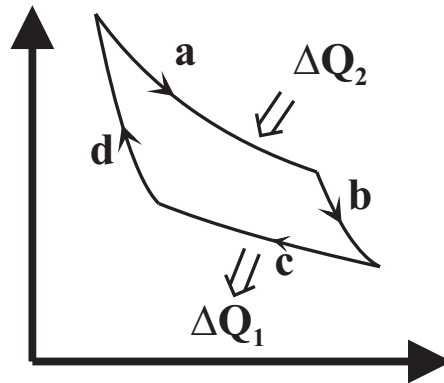For reversible processes the first law can be rewritten as

$$dU = \bar{d}Q - \bar{d}W + \mu\,dN = T\,dS - p\,dV + \mu\,dN.$$

1.8. Carnot cycle

Illustrates the concept of entropy. The Carnot engine $\mathcal{C}$ consists of reversible processes

a)	isothermal	T_2	$\Delta Q_2 > 0$
b)	adiabatic	$T_2 \rightarrow T_1$	$\Delta Q = 0$
c)	isothermal	T_1	$\Delta Q_1 > 0$
d)	adiabatic	$T_1 \rightarrow T_2$	$\Delta Q = 0$

Now $\Delta U = 0$, so $\Delta W = \Delta Q_2 - \Delta Q_1$ (wrong sign here, for simplicity).

We define the *efficiency* as

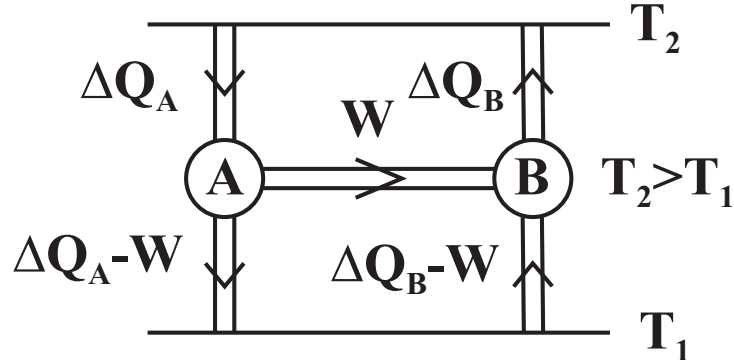$$\eta = \frac{\Delta W}{\Delta Q_2} = 1 - \frac{\Delta Q_1}{\Delta Q_2}.$$

Because the processes are reversible the cycle $\mathcal{C}$ can be reversed and $\mathcal{C}$ works as a heat pump.

Let us consider two Carnot cycles $\mathcal{A}$ and $\mathcal{B}$, for which

$$\Delta W_{\mathcal{A}} = \Delta W_{\mathcal{B}} = \Delta W.$$

$\mathcal{A}$ is an enegine and $\mathcal{B}$ a heat pump. The efficiences are correspondingly

$$\eta_{\mathcal{A}} = \frac{\Delta W}{\Delta Q_{\mathcal{A}}} \text{ and } \eta_{\mathcal{B}} = \frac{\Delta W}{\Delta Q_{\mathcal{B}}}.$$

Let us suppose that

$$\eta_{\mathcal{A}} > \eta_{\mathcal{B}},$$

so that $\Delta Q_{\mathcal{B}} > \Delta Q_{\mathcal{A}}$ or $\Delta Q_{\mathcal{B}} - \Delta Q_{\mathcal{A}} > 0$. The heat would transfer from the cooler reservoir to the warmer one without any other changes, which is in contradiction with the second law (form a). So we must have

$$\eta_{\mathcal{A}} \leq \eta_{\mathcal{B}}.$$

By running the engines backwards one can show that

$$\eta_{\mathcal{B}} \leq \eta_{\mathcal{A}},$$

so that $\eta_{\mathcal{A}} = \eta_{\mathcal{B}}$, i.e. all Carnot engines have the same efficiency.

Note The efficiency does not depend on the realization of the cycle (e.g. the working substance) $\Rightarrow$ The efficiency depends only on the temperatures of the heat reservoirs.
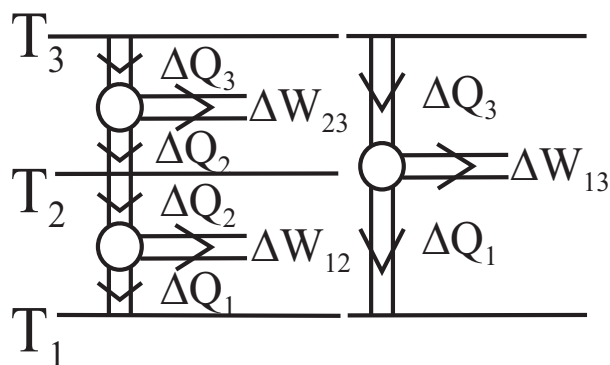
Similarly, one can show that the Carnot engine has the highest efficiency among all engines (also irreversible) working between given temperatures.

Let us consider Carnot's cycle between temperatures T_3 and T_1. Now

$$\eta = 1 - f(T_3, T_1),$$

where

$$f(T_3, T_1) = \frac{\Delta Q_1}{\Delta Q_3}.$$

Here

$$f(T_3, T_2) = \frac{\Delta Q_2}{\Delta Q_3}$$
$$f(T_2, T_1) = \frac{\Delta Q_1}{\Delta Q_2}$$
$$f(T_3, T_1) = \frac{\Delta Q_1}{\Delta Q_3}$$

so

$$f(T_3, T_1) = f(T_3, T_2)f(T_2, T_1).$$

The simplest solution is

$$f(T_2, T_1) = \frac{T_1}{T_2}.$$

We define the *absolute temperature* so that

$$\eta = 1 - \frac{T_1}{T_2}.$$
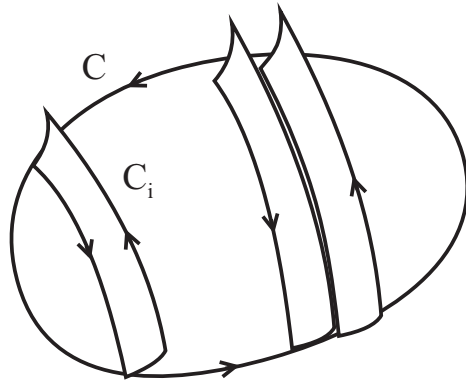
The Carnot cycle satisfies

$$\oint \frac{\mathchar'26 dQ}{T} = 0,$$

since

$$\int_a \frac{\mathchar'26 dQ}{T} = \frac{\Delta Q_2}{T_2}$$

and

$$\int_c \frac{\mathchar'26 dQ}{T} = -\frac{\Delta Q_1}{T_1} = -\frac{\Delta Q_2}{T_2}.$$

This is valid also for an arbitrary reversible cycle

because

$$\oint_C \frac{\mathchar'26 dQ}{T} = \sum_i \oint_{C_i} \frac{\mathchar'26 dQ}{T} = 0.$$

So

$$dS = \frac{\mathchar'26 dQ}{T}$$

is exact and the *entropy* S is a state variable.

Because the Carnot cycle has the highest efficiency a cycle containing irreversible processes satisfies

$$\eta_{\text{irr}} = 1 - \frac{\Delta Q_1}{\Delta Q_2} < \eta_{\text{Carnot}} = 1 - \frac{T_1}{T_2}$$

or

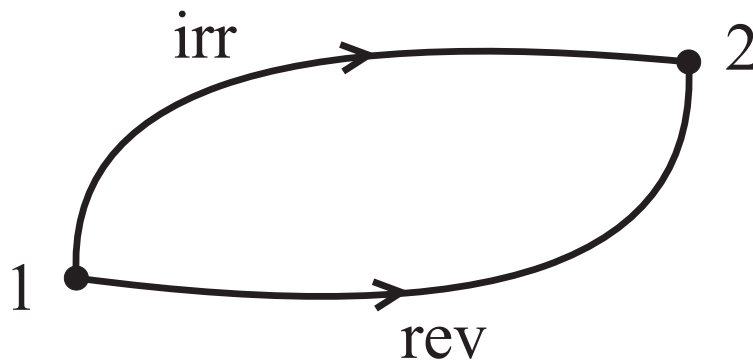$$\frac{\Delta Q_2}{T_2} - \frac{\Delta Q_1}{T_1} < 0.$$

Thus for an arbitrary cycle we have

$$\oint \frac{\bar{d}Q}{T} \leq 0, \qquad\qquad (*)$$

where the equality holds only for reversible processes.

For an arbitrary process $1 \to 2$ the change of the entropy can be obtained from the formula

$$\Delta S = \int_{\text{rev}} dS = \int_{\text{rev}} \frac{\bar{d}Q}{T}.$$

According to the formula $(*)$ we have

$$\int_{\text{irr}} \frac{\bar{d}Q}{T} - \int_{\text{rev}} \frac{\bar{d}Q}{T} < 0,$$

or

$$\Delta S > \int_{\text{irr}} \frac{\bar{d}Q}{T}.$$

This is usually written as

$$dS \geq \frac{\bar{d}Q}{T}$$

and the equality is valid only for reversible processes.

In an isolated system we have

$$\Delta S \geq 0.$$

1.9. 3rd law of thermodynamics

Nernst's law:

$$\lim_{T \to 0} S = 0.$$

A less strong form can be stated as:

When the maximum heat occuring in the process from a state a to a state b approaches zero the also the entropy change $\Delta S_{a \to b} \to 0$.

Note There are systems whose entropy at low temperatures is larger than true equilibria would allow.