
B THERMODYNAMICS

Thermodynamics is the branch of physics that deals with heat, temperature and their relation to energy and work. The relation between these quantities is defined by the four laws of thermodynamics, irrespective of the composition or specific properties of system in question, neither its constituents nor its composition: As such, thermodynamics is incredibly general and finds applications almost everywhere where thermal equilibria are possible and temperatures are defined. Statistical physics is the microscopic theory behind thermodynamics: Here, the actual microscopic properties of a system matter, and under the assumption of thermal equilibrium statistical physics provides a relation between thermodynamic quantities through partition sums. It was the grand accomplishment of Ludwig Boltzmann to realise that thermal energy is energy distributed in the microscopic degrees of freedom of a system if it is fundamentally discrete. With a continuum model of matter one does not have a chance to have this thought, rather, one is forced to think of thermal energy as a "fluid" that can be absorbed by any substance, increasing its temperature.

Systems in thermodynamics are characterised by state variables, which fall into two groups: Extensive state variables are proportional to the amount of matter or the physical size of the system, and include volume V , entropy S , particle number N , electric charge q or magnetisation \mathbf{M} . Each of these state variables has an intensive state variables as a partner that does not depend on the size of the system, for instance the pressure p , the temperature T , the chemical potential μ , the external electric potential Φ and the external magnetic field \mathbf{B} . Extensive and intensive state variables are combined into the Euler-relation, stating that the internal energy U is

$$U = TS - pV + \mu N + \Phi q + \mathbf{B} \cdot \mathbf{M} + \dots \quad (\text{B.8})$$

Changes dU of the internal energy can be introduced by changing the extensive state variables and performing abstract work against the intensive state variables,

$$dU = TdS - pdV + \mu dN + \Phi dq + \mathbf{B} \cdot d\mathbf{M} + \dots \quad (\text{B.9})$$

Commonly, we will restrict ourselves to just three of the terms, $U = TS - pV + \mu N$ and $dU = TdS - pdV + \mu dN$. There are cases where the separation between intensive and extensive state variables is not as clear, for instance in systems with self-interactions, i.e. when the potential is sourced by the electric charge density itself, making it depend on the physical size of the system, too.

B.1 *Ideal classical gases*

The behaviour of an **ideal gas** in terms of the three relevant state variables volume V , pressure p , and temperature T realised as being very dilute, is determined through three relationships: Firstly, the Boyle-Mariotte law, specifying that $pV = \text{const}$ at fixed T , secondly, the Gay-Lussac law, requiring that $V/T = \text{const}$ at fixed p , and thirdly, the Amontons law, making sure that $p/T = \text{const}$ at fixed V . These three statements can be combined into the ideal gas law

$$pV = Nk_{\text{B}}T \quad (\text{B.10})$$

by realising that the combination $pV/T = \text{const} = Nk_{\text{B}}$ is extensive (well, p and T are certainly not extensive but V is) and depends on the amount of substance N .

B.1.1 Van der Waals-gases

The ideal gas law applies only to idealised systems, which are approximated by dilute gases, so the particle density N/V has to be a relevant quantity. In fact, real gases are well described the [van der Waals-equation](#),

$$\left(p + a\left(\frac{N}{V}\right)^2\right) \cdot (V - Nb) = Nk_B T \quad (\text{B.11})$$

with two empirical constants a and b . The second factor is due to the fact that not the entire volume V of a system is accessible by the particles, as they are extended and occupy a tiny but nonzero volume themselves, and the mutual attractive interaction between the particles leads to an effectively higher pressure. Both effects result naturally out of the Lennart-Jones-potential between atoms or molecules with a long-range attractive interaction mediated by electric forces and a short range repulsive force generated by the exclusion principle.

It should be emphasised that the validity of the ideal gas equation or the van der Waals-equation does not rely at all on the existence of atoms or molecules as fundamental constituents, but would be perfectly applicable to a continuum. Then, the particle number N would get replaced by the gas constant R , and the amount of substance is characterised by the number n of moles, $k_B N = Rn$. For a single mole, $n = 1$, suggesting the relation $k_B N_A = R$ with Avogadro's number N_A .

B.1.2 Phenomenological temperature measurements

The ideal gas law can be used to determine temperatures, for instance with Gay-Lussac's law: $T \propto V$ at fixed p , such that a measurement of the volume V is indicative of the temperature T . Surely this measurement is phenomenological as it depends on a particular substance, and furthermore, it is a bit unclear how a measurement of T in one system would change under e.g. Lorentz- or Galilei-transformations. For that purpose, one would like to carry out measurements of temperature mechanically and convert thermal energy into measurable mechanical energy, with a clear transformation behaviour under frame changes: This is achieved by Carnot-engines, as we will see in a second.

It is curious that an ideal gas reaches $V = 0$ at a given pressure at a finite temperature of -273 degrees Celsius, which is set to be the [zero-point of the Kelvin scale](#). Although that temperature can never be reached in practice, it can be determined by means of extrapolation from finite T .

B.2 Zeroth law of thermodynamics

Two systems that are brought into thermal contact exchange thermal energy until they have reached [thermal equilibrium](#) characterised by a common temperature. In thermal equilibrium the flux thermal energy subsides. Typically the time scale of reaching thermal equilibrium (if it is defined at all, there are mind-blowing counter examples) would be determined by the content of thermal energy and the magnitude of heat flux.

Typically, the change δQ in thermal energy Q associated with a change dT in temperature T is related by

$$\delta Q = CdT \quad (\text{B.12})$$

with the heat capacity C . In contrast to the change dT of the state variable, the change in thermal energy depends on how exactly the change in state is achieved: Therefore, it is not an exact differential. The relation $\delta Q = cdT$ served historically as the definition of the calorie by the amount of thermal energy to be added to a quantity of water to raise the temperature by a certain amount.

Thermal energy is proportional to the amount of substance in a system (again, there are counterexamples) and is therefore an extensive quantity unlike temperature. Therefore, it makes sense to define the specific heat c_X

$$C = mc_X \quad (\text{B.13})$$

The index X is meant to illustrate that it matters how the change in state is achieved. For instance, an ideal gas can change the amount of thermal energy that it contains if the temperature is increased, but that increase can be conducted while keeping the pressure p fixed or by keeping the volume V fixed, leading to different results for c_X .

B.2.1 Exact and closed differentials

It is commonly the case in changes in state of a thermodynamical system that it matters how that change in state has been achieved. For instance, an equation state $p(T, V)$ would exhibit a differential change dp

$$dp = \left. \frac{\partial p}{\partial T} \right|_V dT + \left. \frac{\partial p}{\partial V} \right|_T dV \quad (\text{B.14})$$

so that a pressure change can be done increasing the temperature while keeping the volume fixed: In this case, the system would react according to $\left. \frac{\partial p}{\partial T} \right|_V$. Alternatively, the volume can be changed while keeping the temperature fixed, such that $\left. \frac{\partial p}{\partial V} \right|_T$ becomes relevant. Or even more general, one can combine the two changes dT and dV .

When trying to answer the question when exactly a change in state is independent of the way how it has been achieved, the criterion of integrability comes in: If a change in state is path-independent, it only can reflect the initial and final state,

$$F = \int_A^B dF = F(B) - F(A) \quad (\text{B.15})$$

so changing the system from A to B and back to A along a different path should yield zero,

$$\oint dF = 0 \quad (\text{B.16})$$

For a function F with the differential

$$dF = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy = A(x, y)dx + B(x, y)dy \quad (\text{B.17})$$

one can use the Stokes-theorem in an advantageous way and find

$$\oint dF = \oint A(x, y)dx + B(x, y)dy = \int dx dy \left(\frac{\partial B}{\partial x} - \frac{\partial A}{\partial y} \right) \quad (\text{B.18})$$

That integral vanishes if

$$\frac{\partial B}{\partial x} = \frac{\partial A}{\partial y} \quad (\text{B.19})$$

which is made sure by

$$\frac{\partial B}{\partial x} = \frac{\partial^2 F}{\partial x \partial y} = \frac{\partial^2 F}{\partial y \partial x} = \frac{\partial A}{\partial y} \quad (\text{B.20})$$

with the interchangeability of the second partial derivatives according to the Schwarz-theorem. Therefore, the path-independence is made sure by the condition $\partial B/\partial x = \partial A/\partial y$.

In the general case one could imagine a inexact differential

$$\delta F = C(x, y)dx + D(x, y)dy \quad (\text{B.21})$$

without $C = \partial F/\partial x$ nor $D = \partial F/\partial y$, so that $\partial C/\partial y \neq \partial D/\partial x$, and no valid integrability condition applies. In these cases, integrals over δF would become path-dependent and loop integrals will not vanish in general.

B.3 First law of thermodynamics

The foundational idea of the first law of thermodynamics is that **thermal energy** (or heat) is a form of energy: It can be converted to and from other forms of energy, while a global energy conservation law for the sum of all energy forms is fulfilled. For instance, the change dU in internal energy of a system would consist of the changes δW of the mechanical (or electromagnetic) energy content as well as of the change δQ of the thermal energy content:

$$dU = \delta W + \delta Q \quad (\text{B.22})$$

In contrast to the changes δW and δQ , which depend on the exact way in which the change in state is done, the internal energy is conserved: If one takes a system to a certain state and back to the original state along a second path, there can not be any net change in internal energy. Therefore, dU is an exact differential and the path-independence of the changes in state are summarised by

$$\oint dU = 0 \quad (\text{B.23})$$

The conservation of total energy contained in a system as the sum of heat and mechanical energy can be expressed pictorially by the statement, that it is impossible to construct a perpetuum mobile of the first kind: That would be a machine that delivers mechanical work without any changes to its internal state. For the first law of thermodynamics it is irrelevant if the changes in state are performed over a sequence of equilibrium states (called reversible changes) or in an arbitrary way such that not at every instance thermodynamical equilibrium is maintained (called irreversible changes, although we will not deal with those in this course):

$$dU = \delta W_{\text{rev}} + \delta Q_{\text{rev}} = \delta W_{\text{irr}} + \delta Q_{\text{irr}} \quad (\text{B.24})$$

B.3.1 Isochoric changes of state

Let's consider an ideal gas as an example, with state variables T and V , on which the internal energy $U(T, V)$ of the system is thought to depend. Changes dU in the internal energy are given by

$$dU = \left. \frac{\partial U}{\partial T} \right|_V dT + \left. \frac{\partial U}{\partial V} \right|_T dV \quad (\text{B.25})$$

For isochoric changes in state, the volume V is fixed and consequently $dV = 0$. There can not be any work being performed against the pressure, so $\delta W = 0$ and the change in internal energy is necessarily $dU = \delta Q$, such that:

$$\delta Q = \left. \frac{\partial U}{\partial T} \right|_V dT \rightarrow \left. \frac{\partial U}{\partial T} \right|_V = c_V \quad (\text{B.26})$$

leading to the definition of heat capacity at fixed volume V .

B.3.2 Adiabatic changes of state

The situation is very different if one changes the internal energy content of a substance $dU = \delta Q + \delta W$ by increasing the temperature through the addition of thermal energy and simultaneously by performing mechanical work $-pdV$ against the pressure:

$$\delta Q = dU + pdV = \left. \frac{\partial U}{\partial T} \right|_V dT + \left. \frac{\partial U}{\partial V} \right|_T dV + pdV \rightarrow \delta Q = c_V dT + \left(\left. \frac{\partial U}{\partial V} \right|_T + p \right) dV \quad (\text{B.27})$$

in the general case. If, however, the change in state is adiabatic $\delta Q = 0$ and no thermal energy is exchanged for instance through a perfect insulation of the system,

$$c_V dT + \left(\left. \frac{\partial U}{\partial V} \right|_T + p \right) dV = 0 \rightarrow \left. \frac{\partial T}{\partial V} \right|_{\text{ad}} = - \frac{\left. \frac{\partial U}{\partial V} \right|_T + p}{c_V} \quad (\text{B.28})$$

suggesting that the rate at which the temperature changes with changes in the volume is indeed different for the two cases.

B.3.3 Isobaric changes of state

Changing the volume at constant pressure is an isobaric change of state. Then, the volume $V(T, p)$ is dependent on temperature T and pressure p , implying

$$dV = \left. \frac{\partial V}{\partial p} \right|_T dp + \left. \frac{\partial V}{\partial T} \right|_p dT \quad (\text{B.29})$$

where the first term would vanish due to the isobaric condition, $dp = 0$. Defining the specific heat at constant p is then

$$c_p = \left(\frac{\delta Q}{dT} \right) = c_v + \left(\left. \frac{\partial U}{\partial V} \right|_T + p \right) \left. \frac{\partial V}{\partial T} \right|_p \quad (\text{B.30})$$

and is related to the change in temperature with volume by

$$\left(\left. \frac{\partial U}{\partial V} \right|_T + p \right) = (c_p - c_v) \left. \frac{\partial T}{\partial V} \right|_p \quad (\text{B.31})$$

Picking up loose threads in the previous calculation then shows that

$$\left. \frac{\partial T}{\partial V} \right|_{\text{ad}} = -\frac{c_p - c_v}{c_v} \left. \frac{\partial T}{\partial V} \right|_p \quad (\text{B.32})$$

for the adiabatic versus the isobaric change of temperature with volume.

B.3.4 Adiabatic index of a gas

The adiabatic index is the ratio of the heat capacity at constant pressure c_p to heat capacity at constant volume c_v : These two heat capacities are not identical because they correspond to different ways in which energy is added to the system.

$$\frac{c_p}{c_v} = \kappa \quad (\text{B.33})$$

For an ideal gas one can compute the rate of change of temperature with volume at constant pressure to be

$$\frac{p}{Nk_B} = \frac{T}{V} \quad \rightarrow \quad \left. \frac{\partial \ln T}{\partial \ln V} \right|_p = 1 \quad \text{and} \quad \left. \frac{\partial T}{\partial V} \right|_p = \frac{T}{V} \quad (\text{B.34})$$

such that substitution gives

$$\left. \frac{\partial T}{\partial V} \right|_{\text{ad}} = -(\kappa - 1) \frac{T}{V} \quad (\text{B.35})$$

resulting in

$$d \ln T = -(\kappa - 1) d \ln V \quad \text{integrated to} \quad T \sim V^{-(\kappa-1)} \quad \text{or} \quad pV^\kappa = \text{const.} \quad (\text{B.36})$$

An adiabatic process occurs without transfer of heat or mass of substances between a thermodynamic system and its surroundings. In an adiabatic process, energy is transferred to the surroundings only as mechanical work, for instance through $-pdV$, $\mathbf{B} \cdot d\mathbf{M}$ or $\Phi d\rho$.

B.3.5 Entropy

The amount of exchanged thermal energy δQ is not an exact differential as it depends on the particular way in which the change in state has been performed. But it is possible to construct a quantity which is in fact an exact differential: Sticking to our example with $\delta Q = dU + pdV$ as well as $dU = c_V dT$ and an ideal gas with the equation of state $pV = Nk_B T$ suggests that

$$\frac{\delta Q}{T} = c_V \frac{dT}{T} + Nk_B \frac{dV}{V} \quad (\text{B.37})$$

is an exact differential called dS ,

$$dS \equiv \frac{\delta Q}{T} \rightarrow S(T, V) = \int_{T_0}^T c_V \frac{dT}{T} + nk_B \int_{V_0}^V \frac{dV}{V} \quad (\text{B.38})$$

provided that the first term only depends on T and the second term only on V . While this is clear for the second term, it is made sure for the first term by Boyle's experiment showing that the specific heat c_V does only depend on T : For $U(T, V)$ the differential reads

$$dU = \left. \frac{\partial U}{\partial T} \right|_V dT + \left. \frac{\partial U}{\partial V} \right|_T dV \quad (\text{B.39})$$

c_V is defined as the change of internal energy with temperature and corresponds to the first term. Boyle observed that in having an isolated gas expand into a larger volume the temperature does not change: Insolation implies that the change dU of internal energy must be zero, and the empirical observation of $dT = 0$ then suggests that the internal energy can not depend on volume (although we can not know that yet, makes a lot of sense because internal energy in a gas is the kinetic energy of the particles, and that would obviously not depend on volume):

$$dU = \left. \frac{\partial U}{\partial V} \right|_T dV = 0 \quad (\text{B.40})$$

Therefore, internal energy is a function of temperature alone, and so is c_V .

S is called the [entropy](#) and the differential dS is exact,

$$\oint dS = 0 \quad (\text{B.41})$$

so that a cyclic change of state always results in a zero change in entropy, and the change in entropy does not depend on the way a change in state is done, in contrast to δQ or δW . Please keep in mind that we do not deal with irreversible changes in state, as they proceed along non-equilibrium states and temperature would not be defined at every instance.

B.4 Second law of thermodynamics

After the realisation that mechanical energy can be converted into thermal energy and vice versa, and that there is a corresponding energy conservation law for the total internal energy U , it should be clarified to what extent thermal energy can be transformed back into mechanical energy; after all, it is clear that mechanical energy can be completely converted into thermal energy, for instance by friction.

The [second law](#) states that an engine, which works in cycles and returns to its initial state after performing each cycle (so that no energy is stored somehow in the engine) is not allowed to perform mechanically usable work by just cooling down an energy reservoir: It is impossible to gain mechanical work out of thermal equilibrium. One can, however, construct engines that convert thermal energy into mechanical energy, but they require energy reservoirs at two different temperatures and a temperature non-equilibrium. Ideally, those Carnot-engines are able to convert thermal energy into mechanical work, at a given conversion efficiency (that only depends on the temperatures) which is strictly smaller than unity (as long as we're dealing with positive absolute temperatures, we'll revisit this amazingly interesting point later).

B.4.1 Conversion from thermal to mechanical energy

The [Carnot-engine](#) is the prime example of an idealised thermodynamical engine, which can use mechanical energy to pump thermal energy from a cold reservoir to a hot reservoir against the natural tendency of thermal energy to flow from hot to cold, or it can be used to gain mechanical energy from the flux of thermal energy from a hot reservoir to a cold reservoir. A Carnot-engine is working in a cyclic fashion, so it does not retain any energy for itself and returns exactly back to its initial state.

One possible realisation of a Carnot-engine is a series of isothermal and adiabatic changes of state of an ideal gas at two different temperatures: The engine absorbs a quantity Q_1 at temperature T_1 from the hot reservoir, and passes a lower quantity Q_2 of thermal energy onto the cold reservoir at temperature T_2 , possibly delivering work W . I'd like to emphasise that is any number of possible Carnot-engines, with the common property that they absorb thermal energy in a reversible way: Because dS is an exact differential,

$$\oint dS = \oint \frac{\delta Q}{T} = 0 \quad \rightarrow \quad \frac{Q_1}{T_1} = \frac{Q_2}{T_2} \quad (\text{B.42})$$

Energy conservation implies that $Q_1 = W + Q_2$ and therefore for the efficiency η of the Carnot-engine

$$\eta = \frac{W}{Q_1} \left(1 - \frac{T_2}{T_1} \right) \quad (\text{B.43})$$

For the case of thermal equilibrium, $T_2 = T_1$, $\eta = 0$ and $W = 0$, so no mechanical work can be performed. All Carnot engines necessarily run at the same efficiency: If you construct a system where the first engine gains work by having heat flow from T_1 to T_2 and use that work for powering a second engine to reverse the heat flow, both the heat flows and the flow of mechanical work should be perfectly balanced and no net changes can be observed: Otherwise, the more efficient engine would deliver mechanical work while no changes in temperature are observed, in contradiction with the second law of thermodynamics.

A highly unusual Carnot-engine is the **ratchet and pawl-engine**: A propeller is set into motion by impacting air molecules, but a ratchet-mechanism only allows it to turn into a single direction. Then one could use the thermal energy contained in the unordered motion of the air molecules to turn the propeller and possibly lift a weight, thus performing mechanical energy. If that was possible, one would have converted thermal energy into mechanical energy in a perfect way, so there must be a catch. So, for turning the contraption one needs to disengage the ratched by investing δ as an energy in addition to the energy ϵ for lifting the weight, supplied at temperature T_1 of the air. But the ratchet might just disengage randomly, when the energy δ might be randomly supplied by an impacting air molecule, possibly at a different temperature T_2 . The probabilities for both cases to happen are given by Boltzmann-probabilities:

$$\exp\left(-\frac{\epsilon + \delta}{k_B T_1}\right) = \exp\left(-\frac{\delta}{k_B T_2}\right) \rightarrow \frac{\epsilon}{\delta} = \eta = 1 - \frac{T_2}{T_1} \quad (\text{B.44})$$

so that the engine runs at the Carnot-efficiency, and at $\eta = 0$ in thermal equilibrium $T_1 = T_2$. In this context reversibility implies that the universally applicable Boltzmann-probabilities are characterised by temperature only: If that changes, they probabilities adjust at once, and there is no lag of the machine to a change in T . I find it very funny to imagine that both the idealised steam engine and the ratchet and pawl-machine operate at the same efficiency: Plugging them together such that the ratchet uses the work provided by the steam engine heats up the air at the propeller relative to the ratchet in exactly the proportion that is used by the steam engine to perform work from the non-equilibrium between propeller and ratchet.

B.4.2 Generalised Carnot-engines

Carnot-engines do not have to be constructed in a specific way: Neither do they need a specific substance like the ideal gas, nor is the term by which mechanical energy is gained pdV , and the ratchet and pawl-machine is a cute example for that; reversibility as a condition is enough. All Carnot-engines operate at the same fundamental efficiency, which can only be a function of the two temperatures

$$Q_2 = Q_1 f(T_1, T_2) \quad (\text{B.45})$$

with efficiency:

$$\eta = 1 - f(T_1, T_2) \quad (\text{B.46})$$

To get some insight into the functional form of f one can build a chain of two Carnot engines, the first one links a reservoir at T_1 with a second reservoir at T_2 ; it takes in an amount Q_1 of thermal energy, generates mechanical work W and dumps Q_2 into the second reservoir: $W = Q_1(1 - f(T_1, T_2))$ with the wasted thermal energy $Q_2 = Q_1 f(T_1, T_2)$. Then, a second Carnot-engine absorbs exactly Q_2 at T_2 , generates W' in work and passes Q_3 onto T_3 : $W' = Q_2(1 - f(T_2, T_3))$ with the wasted thermal energy $Q_3 = Q_2 f(T_2, T_3)$.

☞ Carnot-engines are mechanical devices to measure temperatures, they convert thermal to mechanical energy at a fixed efficiency that only depends on the temperatures.

The sum of mechanical work $W + W' = Q_1(1 - f(T_1, T_2))f(T_2, T_3)$,

$$W + W' = Q_1(1 - f(T_2, T_3)) \quad (\text{B.47})$$

needs to be equal to that of an imaginary Carnot-engine linking the first and the third reservoir directly, i.e. one needs to have transitivity in the efficiencies:

$$f(T_1, T_2) \cdot f(T_2, T_3) = f(T_1, T_3) \quad (\text{B.48})$$

Taking the logarithm of the transitivity relation

$$\ln f(T_1, T_2) + \ln f(T_2, T_3) = \ln f(T_1, T_3) \quad (\text{B.49})$$

and computing the derivative $\partial/\partial T_1$ yields

$$\frac{\partial}{\partial T_1} \ln f(T_1, T_2) = \frac{\partial}{\partial T_1} \ln f(T_1, T_3) \quad (\text{B.50})$$

with $f(T_2, T_3)$ dropping out as it does not depend on T_1 . Such a differential equation suggest a separation ansatz $\ln f(T_1, T_2) = A(T_1) + B(T_2)$ because both sides of the equation need to be proportional to the same function in T_1 and the differentiation can not mix in a dependence on the other variable. Reverting the logarithm this would then imply $f(T_1, T_2) = A(T_1) \cdot B(T_2)$ and transitivity is naturally fulfilled if $A(T_2) = 1/B(T_2)$. Substituting back gives

$$f(T_1, T_2) = \frac{B(T_2)}{B(T_1)} \quad (\text{B.51})$$

and for the efficiency

$$\eta = 1 - \frac{B(T_2)}{B(T_1)} \quad (\text{B.52})$$

Therefore, we would call $B(T)$ the thermodynamic temperature as measured by the Carnot-engine: It is a bit circumstantial at this point that it corresponds to the temperature T measured with Boyle's law in an ideal gas. Carnot-engines measure temperature differences or ratios only, so one needs to have a reference point relative to which actual temperatures are determined: $T = 0$ would be an obvious attractive choice from a practical point of view, but there, the Carnot-efficiency η would be undefined! The common definition is taken to be the triple point of water. At a temperature of $T = 273.15$ K and at a pressure of $p = 611.657$ Pa the solid, liquid and gaseous state of water exist simultaneously which is easy to observe.

B.4.3 Entropy and energy conversion

The amounts of thermal energy Q_i exchanged with the heat baths at temperature T_i follow the relation

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \quad (\text{B.53})$$

for any Carnot engine operating between two reservoirs. In the continuum limit this implies

$$\sum_i \frac{\delta Q_i}{T_i} = 0 \quad (\text{B.54})$$

for a chain of Carnot engines, while the usable mechanical work is given by

$$W = \sum_i \delta Q_i \quad (\text{B.55})$$

but we need to invest mechanical work W' to put the amount of δQ_i back into the reservoir i at temperature T_i :

$$W' = \sum_i \delta Q_i \frac{T_i - T_n}{T_i} = \sum_i \delta Q_i - T_n \sum_i \frac{\delta Q_i}{T_i} \quad (\text{B.56})$$

so that the net gain is:

$$W - W' = T_n \sum_i \frac{\delta Q_i}{T_i} \quad (\text{B.57})$$

with $W = W'$ for a loop. Therefore,

$$\sum_i \frac{\delta Q_i}{T_i} \rightarrow \oint \frac{dQ}{T} = \oint dS = 0 \quad (\text{B.58})$$

showing the consistency between the Carnot-efficiency and the exactness of the entropy differential dS . Substituting $dS = \delta Q/T$ into the first law of thermodynamics yields

$$dU = \delta Q + \delta W = TdS - pdV \quad (\text{B.59})$$

where we could replace the inexact differential δQ with the exact dS , introducing T as the function that makes it integrable or exact. The corresponding Euler-relation then assumes the form $U = TS - pV + \mu N + \dots$

B.4.4 Irreversible processes and entropy increase in closed systems

Typically, the net change in entropy in a reversible change in state is zero, $dS = 0$. But when for instance to systems with different temperature are brought into thermal contact, the first law of thermodynamics requires that there is a flow of thermal energy from the hot to the cold body, equilibrating their temperatures. That process happens spontaneously as a consequence of disequilibrium, and the **entropy will increase**.

From the first law of thermodynamics and from the definition of entropy as an exact differential one gets

$$dU = TdS \quad \rightarrow \quad dS = \frac{dU}{T} \quad (\text{B.60})$$

Defining the specific heat $dU = cdT$ allows us to write the entropy differential as

$$dS = c \frac{dT}{T} = cd \ln T \quad \text{with the solution} \quad S = c \ln T + S_0 \quad (\text{B.61})$$

where S_0 is an integration constant. Comparing the entropy before thermal contact

$$S_i = c(\ln T_1 + \ln T_2) \quad (\text{B.62})$$

with that after thermal contact:

$$S_f = 2c \ln \left(\frac{T_1 + T_2}{2} \right) \quad (\text{B.63})$$

shows that the difference in entropy is in fact positive,

$$\Delta S = S_f - S_i = c \cdot \left[2 \ln \left(\frac{T_1 + T_2}{2} \right) - (\ln T_1 + \ln T_2) \right] \geq 0 \quad (\text{B.64})$$

because of Jensen's inequality.

B.4.5 Concave functions and Legendre transforms

One has the freedom to replace state functions by performing **Legendre transforms**. The integration of the entropy into the Euler-relation would only be sensible a replacement of S by T and vice versa can be done in a defined way, and for that entropy needs to be a convex or concave function of T : Then, the Legendre-transform is defined yielding a concave or convex function in return, so that the inverse Legendre-transform is defined just as well.

In general, convex functions obey the inequality

$$g(\theta x + (1 - \theta)y) \geq \theta g(x) + (1 - \theta)g(y) \quad (\text{B.65})$$

for every value of θ . For the particular choice of $\theta = 1/2$ and the logarithm $g(x) = \ln x$ one gets:

$$\ln \left(\frac{x + y}{2} \right) \geq \frac{1}{2} (\ln x + \ln y) \quad (\text{B.66})$$

By comparison with eqn.B.64 one immediately recognises that the entropy is a convex function of T .

Furthermore, by writing $dU = TdS$ as the first term in the differential Euler-relation and noticing that typically the internal energy is proportional to temperature and the amount of matter a system is composed of, $dU = CdT$ with the heat capacity C , one realises that entropy should (normally, again, there might be counterexamples) be extensive, and can be paired with temperature T as an intensive quantity.

B.5 Third law of thermodynamics

There is a rather obscure **third law of thermodynamics**, which determines the zero-point of entropy: As we are only concerned with changes in the thermodynamic variables and potentials only differences matter, and there is a priori no reference relative to which entropy is measured, unlike temperature T or any form of energy.

Therefore, one postulates that the entropy takes on a constant value, possibly to be set to zero, as the temperature approaches absolute zero.