Chapter 4
The Second Law of Thermodynamics

4.1 The Second Law

In our qualitative description of processes we have already emphasized the trend of any isolated system towards an unique and stable equilibrium state. The *Second Law of Thermodynamics* is the quantitative formulation of this observation. Its importance goes well beyond the computation of the unique equilibrium states for isolated systems. In particular, as will be seen, it gives strong restrictions for the efficiency of energy conversion systems, and thus is of enormous importance for engineering applications.

The original derivation of the second law through Rudolf Clausius (1822–1888) was based on the argument that the direction of heat transfer is restricted and then relied heavily on statements on thermodynamic cycles. The following derivation postulates an inequality to describe the trend to equilibrium, and uses arguments on process direction for simple equilibration processes to identify terms in the postulated equation. This approach allows us to introduce the second law quite early, before any thermodynamic processes and cycles are discussed. With this, entropy and the second law will be available for the evaluation of processes and cycles from the start. All equations and conclusions agree to the classical approach, as presented in most textbooks on engineering thermodynamics, just the order of arguments is different.

4.2 Entropy and the Trend to Equilibrium

To set the stage, we briefly summarize our earlier statements on processes in closed systems: a closed system can be manipulated by exchange of work and heat with its surroundings only. In non-equilibrium—i.e., irreversible—processes, when all manipulation stops, the system will undergo further changes until it reaches a final equilibrium state. This equilibrium state is stable, that is the system will not leave the equilibrium state spontaneously.

H. Struchtrup, *Thermodynamics and Energy Conversion*,
DOI: 10.1007/978-3-662-43715-5_4,

It requires new action—exchange of work or heat with the surroundings—to change the state of the system.

The following non-equilibrium processes are well-known from experience, and will be used in the considerations below: (a) Heat goes from hot to cold. When two bodies at different temperatures are brought into thermal contact, heat will flow from the hotter to the colder body until both reach their common equilibrium temperature. (b) Work can be transferred without restriction, by means of gears and levers. However, in transfer some work might be lost to friction.

The process from an initial non-equilibrium state to the final equilibrium state requires some time. However, if the actions on the system (only work and heat!) are sufficiently slow, the system has enough time to adapt and will be in equilibrium states at all times. We speak of quasi-static—or, reversible—processes. When the slow manipulation is stopped at any time, no further changes occur.

The behavior of isolated systems described above—a change occurs until a stable state is reached—can be described mathematically by an inequality. The final stable state must be a maximum (alternatively, a minimum) of a suitable extensive property describing the system. We call that extensive property *entropy*, denoted S, and write an inequality for the isolated system,

$$\frac{dS}{dt} = \dot{S}_{gen} \geq 0 \; . \tag{4.1}$$

$\dot{S}_{gen}$ is called the *entropy generation rate*. The entropy generation rate is positive in non-equilibrium ($\dot{S}_{gen} > 0$), and vanishes in equilibrium ($\dot{S}_{gen} = 0$). The new equation (4.1) states that in an isolated system the entropy will grow in time ($\frac{dS}{dt} > 0$) until the stable equilibrium state is reached ($\frac{dS}{dt} = 0$). Non-zero entropy generation describes the irreversible process towards equilibrium, e.g., through internal heat transfer and friction. There is no entropy generation in equilibrium. Since entropy only grows before the equilibrium state is reached, the latter is a maximum of entropy.

The above postulation of an inequality is based on phenomenological arguments. The discussion of irreversible processes has shown that all isolated systems will in time evolve to a unique equilibrium state. The first law alone does not suffice to describe this behavior. We have seen this in the description of temperature equilibration in Sec. 3.12, where the first law has infinitely many solutions for the final temperatures T_A, T_B, and additional input is needed to state that $T_A = T_B$ in equilibrium. Above, we relied on experience as additional input, the second law is a formalization of that experience. Non-equilibrium processes aim to reach equilibrium, and the inequality is required to describe the clear direction in time.

In the next sections we will extend the second law to non-isolated system, and identify entropy as a measurable property.

4.3 Entropy Flux

In non-isolated systems, which exchange heat and work with the surroundings, we expect an exchange of entropy with the surroundings which must be added to the entropy inequality. We write

$$\frac{dS}{dt} = \dot{\Psi} + \dot{S}_{gen}, \quad \text{with } \dot{S}_{gen} \geq 0 \ , \tag{4.2}$$

where $\dot{\Psi}$ is the *entropy flux*. This equation states that the change of entropy in time (dS/dt) is due to transport of entropy over the system boundary ($\dot{\Psi}$) and generation of entropy within the system boundaries ($\dot{S}_{gen}$). This form of the second law is valid for all processes in closed systems. The entropy generation rate is positive, $\dot{S}_{gen} > 0$, for irreversible processes, and it vanishes, $\dot{S}_{gen} = 0$, in equilibrium, and for reversible processes, where the system is in equilibrium states at all times.

All real technical processes are somewhat irreversible, since friction and heat transfer cannot be avoided. Reversible processes are idealizations that can be used to study the principle behavior of processes, and best performance limits.

Since a closed system can only be manipulated through the exchange of heat and work with the surroundings, the transfer of any other property, including the transfer of entropy, must be related to heat and work, and must vanish when heat and work vanish. Therefore the entropy flux $\dot{\Psi}$ can only be of the form

$$\dot{\Psi} = \beta \dot{Q} - \gamma \dot{W} \ , \tag{4.3}$$

with coefficients β, γ that must be related to system and process properties.

Equation (4.2) gives the mathematical formulation of the trend to equilibrium for a non-isolated closed system (exchange of heat and work, but not of mass). The next step is to identify entropy S and the coefficients β, γ in the entropy flux $\dot{\Psi}$ in terms of quantities we can measure or control.

4.4 Entropy in Equilibrium

For quasi-static processes, which are in equilibrium states at all times, the entropy generation vanishes, $\dot{S}_{gen} = 0$, and the equation (4.2) for entropy becomes

$$\frac{dS}{dt} = \dot{\Psi} \ ; \tag{4.4}$$

in quasi-static processes the entropy of a closed system changes by entropy transfer only.

With this and (4.3), we have for reversible processes, where $\dot{W} = p\frac{dV}{dt}$,

$$\frac{dS}{dt} = \beta \dot{Q} - \gamma p \frac{dV}{dt} \ . \tag{4.5}$$

Eliminating heat $\dot{Q}$ between this, and the first law for quasi-static processes (3.13), $\frac{dU}{dt} = \dot{Q} - p\frac{dV}{dt}$, yields

$$\frac{dS}{dt} = \beta \frac{dU}{dt} + (\beta - \gamma)\, p \frac{dV}{dt} \;. \tag{4.6}$$

This equation relates entropy S to the state properties U and V, and implies that $S(U, V)$ is a state property as well. Since pressure p, volume V, temperature T, and internal energy U are related through the thermal and caloric equations of state, $p = p(T, V)$, $U = U(T, V)$, the knowledge of any two of these determines the others. Thus, entropy, our new property, can be written as a function of any two of the above properties, e.g., $S(T, V)$ or $S(p, T)$ or $S(U, p)$ or $S(U, V)$. From the last form, we compute the time derivative of entropy with the chain rule,

$$\frac{dS}{dt} = \left(\frac{\partial S}{\partial U}\right)_V \frac{dU}{dt} + \left(\frac{\partial S}{\partial V}\right)_U \frac{dV}{dt} \;. \tag{4.7}$$

Comparison of the last two equations relates β and $(\beta - \gamma)$ to the partial derivatives of entropy,

$$\left(\frac{\partial S}{\partial U}\right)_V = \beta \quad , \quad \left(\frac{\partial S}{\partial V}\right)_U = (\beta - \gamma)\, p \;. \tag{4.8}$$

So far, entropy and the coefficients β and γ in the entropy flux are not yet fixed. Since entropy is a state property, also its derivatives $\left(\frac{\partial S}{\partial U}\right)_V$ and $\left(\frac{\partial S}{\partial V}\right)_U$ are state properties, and it follows that β and $(\beta - \gamma)$ are state properties as well.[1] Since S, U and V are extensive, their quotients and derivatives must be intensive quantities; therefore β and γ are intensive quantities. Obviously, we are interested in non-trivial entropy functions, and therefore we must have $\beta \neq 0$, $(\beta - \gamma) \neq 0$.

In anticipation of later discussion we introduce the *thermodynamic temperature* as $T = 1/\beta$. At this point, this is a just a definition, however, it will be shown soon that T has all the characteristics required for the definition of a thermodynamic temperature. In particular, it will be seen that the entropy flux term $\beta\dot{Q} = \dot{Q}/T$ is related to the restriction of the direction of heat transfer: heat flows from warm to cold, not vice versa. No such restriction applies for work, which, by means of gears and levers, can be transmitted from slow to fast and vice versa, or from low force to high force and vice versa. Because of this, γ must be a constant, which can be set to $\gamma = 0$—the interested reader will find the full argument in Sec. 4.17.

With $\beta = 1/T$ and $\gamma = 0$, we have the partial derivatives of entropy expressed through measurable quantities,

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[1] Note that, when the entropy flux (4.3) was introduced, this was not clear: β and $(\beta - \gamma)$ could in principle depend on work and heat. The argument presented here shows that this is not so, at least in equilibrium.

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \quad , \quad \left(\frac{\partial S}{\partial V}\right)_U = \frac{p}{T} \, . \tag{4.9}$$

The entropy flux (4.3) is

$$\dot{\Psi} = \frac{\dot{Q}}{T} \, . \tag{4.10}$$

4.5 Entropy as Property: The Gibbs Equation

With the partial derivatives of entropy as above, the differential $dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$ becomes

$$TdS = dU + pdV \, . \tag{4.11}$$

This relation is known as the Gibbs equation, named after Josiah Willard Gibbs (1839 - 1903). The Gibbs equation is a differential relation between properties and valid for *all* simple substances.

Since T and p are intensive, and U and V are extensive properties, entropy is extensive. The specific entropy $s = S/m$ can be computed from the Gibbs equation for specific properties, which is obtained by division of (4.11) with the constant mass m,

$$Tds = du + pdv \, . \tag{4.12}$$

Replacing internal energy by enthalpy, $u = h - pv$, gives an alternative form of the Gibbs equation,

$$Tds = dh - vdp \, . \tag{4.13}$$

The Gibbs equation gives a large number of relations and restrictions between properties, in particular it allows to determine property relations for entropy.

Entropy, just as internal energy, cannot be measured directly. Property relations for entropy are computed from the Gibbs equation, and the thermal and caloric equations of state, $p\,(T, v)$ and $u\,(T, v)$. Here, we consider this for incompressible substances and for ideal gases.

For incompressible liquids and solids, the specific volume is constant, hence $dv = 0$. The caloric equation of state (3.18) implies $du = cdT$ and the Gibbs equation reduces to $Tds = cdT$. For constant specific heat, $c = const.$, integration gives entropy as explicit function of temperature,

$$s\,(T) = c \ln \frac{T}{T_0} + s_0 \, , \tag{4.14}$$

where s_0 is the entropy at the reference temperature T_0. As long as no chemical reactions are involved, the definition of the entropy scale, i.e., the value of s_0, can be freely chosen; the third law of thermodynamics will fix the scale properly.

For an ideal gas we have $du = c_v dT$ and $v = RT/p$ so that the Gibbs equation (4.13) becomes

$$ds = c_p \frac{dT}{T} - R\frac{dp}{p} \ . \tag{4.15}$$

For a gas with temperature dependent specific heat, integration yields

$$s\left(T,p\right) = s^0\left(T\right) - R\ln\frac{p}{p_0} \ , \tag{4.16}$$

where

$$s^0\left(T\right) = \int_{T_0}^{T} \frac{c_p\left(T'\right)}{T'} dT' + s_0 \tag{4.17}$$

is the—temperature dependent—entropy at reference pressure p_0, and s_0 is the reference entropy at $\{T_0, p_0\}$.

For a gas with constant specific heat, the integration can be performed to give

$$s\left(T,p\right) = c_p \ln\frac{T}{T_0} - R\ln\frac{p}{p_0} + s_0 \ . \tag{4.18}$$

The entropy $s\left(T,v\right)$ follows from this either by replacing the pressure with the ideal gas equation ($p = RT/v$) or from integrating (4.12) as (for constant specific heat)

$$s\left(T,v\right) = c_v \ln\frac{T}{T_0} + R\ln\frac{v}{v_0} + s_0 \tag{4.19}$$

Property relations for other substances will be presented in Chapter 6.

4.6 T-S-Diagram

Solving the first law for reversible processes (3.13) for heat and comparing the result with the Gibbs equation we find, with $\dot{Q}dt = \delta Q$,

$$dS = \frac{1}{T}\left(dU + pdV\right) = \frac{1}{T}\delta Q \ . \tag{4.20}$$

We recall that heat is a path function, i.e., δQ is an inexact differential, but entropy is a state property, i.e., dS is an exact differential. In the language of mathematics, the inverse thermodynamic temperature $\frac{1}{T}$ serves as an integrating factor for δQ, such that $dS = \frac{1}{T}\delta Q$ becomes an exact differential.

From the above, we see that for reversible processes $\delta Q = TdS$. Accordingly, the total heat exchanged in a reversible process can be computed from temperature and entropy as the area below the process curve in the temperature-entropy diagram (T-S-diagram),

$$Q_{12} = \int_1^2 TdS \ . \tag{4.21}$$

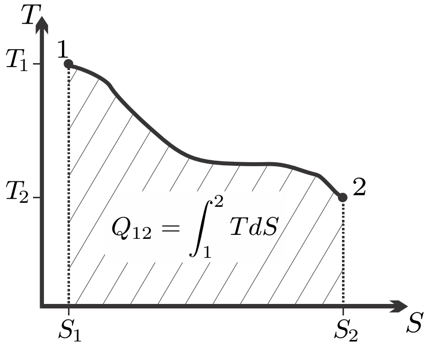

Fig. 4.1 Heat as the area below the reversible process curve in the T-S-diagram

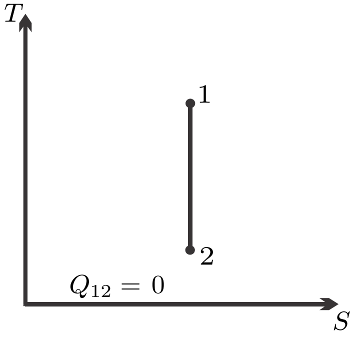

Fig. 4.2 Isentropic (adiabatic reversible) process in the T-S-diagram

This is analog to the computation of the work as $W_{12} = \int_1^2 pdV$, Fig. 4.1 gives an illustration.

For a reversible adiabatic process $\delta Q = TdS = 0$, that is the entropy is constant in the process. We say a reversible adiabatic process is *isentropic*. The process curve in the T-S-diagram is a vertical line, see Fig. 4.2.

4.7 The Entropy Balance

In the previous sections, we considered homogeneous systems that undergo equilibrium processes. To generalize for processes in inhomogeneous systems, we consider the system as a compound of sufficiently small subsystems. The key assumption is that each of the subsystems is in local equilibrium, so that it can be characterized by the same state properties as a macroscopic equilibrium system. To simplify the proceedings somewhat, we consider numbered subsystems of finite size, and summation. A more refined argument would consider infinitesimal cells dV, and integration.

Figure 4.3 indicates the splitting into subsystems, and highlights a subsystem i inside the system and a subsystem k at the system boundary. Temperature and pressure in the subsystems are given by T_i, p_i and T_k, p_k, respectively. Generally, temperature and pressure are inhomogeneous, that is adjacent subsystems have different temperatures and pressures. Accordingly, each subsystem interacts with its neighborhood through heat and work transfer as indicated by the arrows. Heat and work exchanged with the surroundings of the system are indicated as $\dot{Q}_k$ and $\dot{W}_k$.

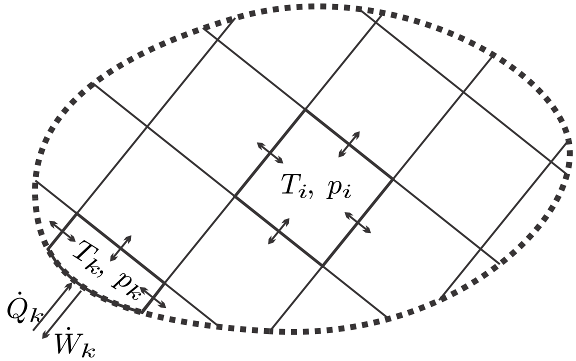

Fig. 4.3 Non-equilibrium system split into small equilibrium subsystems. Arrows indicate work and heat exchange between neighboring elements, and the surroundings.

Internal energy and entropy in a subsystem i are denoted as E_i and S_i, and, since both are extensive, the corresponding quantities for the complete system are obtained by summation over all subsystems, $E = \sum_i E_i$, $S = \sum_i S_i$. Note that in the limit of infinitesimal subsystems the sums become integrals, as in Sec. 2.7. The balances of energy and entropy for a subsystem i read

$$\frac{dE_i}{dt} = \dot{Q}_i - \dot{W}_i \quad , \quad \frac{dS_i}{dt} = \frac{\dot{Q}_i}{T_i} + \dot{S}_{gen,i} \ , \tag{4.22}$$

where $\dot{Q}_i = \sum_j \dot{Q}_{i,j}$ is the net heat exchange, and $\dot{W}_i = \sum_j \dot{W}_{i,j}$ is the net work exchange for the subsystem. Here, the summation over j indicates the exchange of heat and work with the neighboring cells, such that, e.g., $\dot{Q}_{i,j}$ is the heat that i receives from the neighboring cell j.

To obtain first and second law for the compound system, we have to sum the corresponding laws for the subsystems, which gives

$$\frac{dE}{dt} = \dot{Q} - \dot{W} \quad \text{with} \quad \dot{Q} = \sum_k \dot{Q}_k \ , \ \dot{W} = \sum_k W_k \tag{4.23}$$

and

$$\frac{dS}{dt} = \sum_k \frac{\dot{Q}_k}{T_k} + \dot{S}_{gen} \quad \text{with} \quad \dot{S}_{gen} \geq 0 \ . \tag{4.24}$$

In the above $\dot{Q}_k$ is the heat transferred over a system boundary which has temperature T_k. As will be explained next, the summation over k concerns only heat and work exchange with the surroundings.

Since energy is conserved, the internal exchange of heat and work between subsystems cancels in the conservation law for energy (4.23). For instance, in the exchange between neighboring subsystems i and j, $Q_{i,j}$ is the heat that i receives from j and $W_{i,j}$ is the work that i does on j. Moreover, $Q_{j,i}$ is the heat that j receives from i and $W_{j,i}$ is the work that j does on i. Since energy is conserved, no energy is added or lost in transfer between i and j, that is $Q_{i,j} = -Q_{j,i}$ and $W_{i,j} = -W_{j,i}$. Accordingly, the sums vanish, $Q_{i,j} + Q_{j,i} = 0$ and $W_{i,j} + W_{j,i} = 0$. Extension of the argument shows that the internal exchange of heat and work between subsystems adds up to zero, so that only exchange with the surroundings, indicated by subscript k, appears in (4.23).

Entropy, however, is not conserved, but may be produced. Exchange of heat and work between subsystems, if irreversible, will contribute to the entropy generation rate $\dot{S}_{gen}$. Thus, the total entropy generation rate $\dot{S}_{gen}$ of the compound system is the sum of the entropy generation rates in the subsystems $\dot{S}_{gen,i}$ plus additional terms related to the energy transfer between subsystems, $\dot{S}_{gen} = \sum_i \dot{S}_{gen,i} + \sum_{i,j} \frac{\dot{Q}_{i,j}}{T_i}$. In simple substances, entropy generation occurs due to internal heat flow and internal friction. We repeat that entropy generation is strictly positive, $\dot{S}_{gen} > 0$, in irreversible processes, and is zero, $\dot{S}_{gen} = 0$, in reversible processes.

To fully quantify entropy generation, that is to compute its actual value, requires the detailed local computation of all processes inside the system from the conservation laws and the second law as partial differential equations. The derivation and analysis of the local laws is a topic of *Non-equilibrium Thermodynamics.*

The above derivation of the second law equation (4.24) relies on the assumption that the equilibrium property relations for entropy are valid locally also for non-equilibrium systems. This local equilibrium hypothesis—equilibrium in a subsystem, but not in the compound system—works well for most systems in technical thermodynamics. It should be noted that the assumption breaks down for extremely strong non-equilibria; this lies outside the scope of our endeavours.

4.8 The Direction of Heat Transfer

A temperature reservoir is defined as a large body whose temperature does not change when heat is removed or added. Figure 4.4 shows heat transfer between two reservoirs of temperatures T_H and T_L, where T_H is the

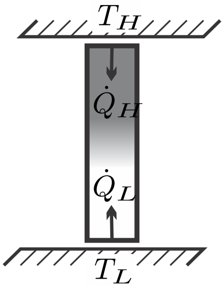

Fig. 4.4 Heat transfer between two reservoirs at T_1 and T_2. In steady state the heat conductor does not accumulate energy, therefore $\dot{Q}_L = -\dot{Q}_H$.

temperature of the hotter system. The heat is transferred through a heat conductor, which is the thermodynamic system to be evaluated. A pure heat transfer problem is studied, where the conductor receives the heat flows $\dot{Q}_H$ and $\dot{Q}_L$, and exchanges no work with the surroundings, $\dot{W} = 0$. The first and second law (4.23, 4.24) applied to the heat conductor read

$$\frac{dU}{dt} = \dot{Q}_L + \dot{Q}_H \quad , \quad \frac{dS}{dt} - \frac{\dot{Q}_L}{T_L} - \frac{\dot{Q}_H}{T_H} = \dot{S}_{gen} \geq 0 \ . \tag{4.25}$$

For steady state conditions no changes over time are observed in the conductor, so that $\frac{dU}{dt} = \frac{dS}{dt} = 0$. The first law shows that the heat fluxes must be equal in absolute value, but opposite in sign,

$$\dot{Q}_H = -\dot{Q}_L = \dot{Q} \ . \tag{4.26}$$

With this, the second law reduces to the inequality

$$\dot{Q}\left(\frac{1}{T_L} - \frac{1}{T_H}\right) = \dot{S}_{gen} \geq 0 \ . \tag{4.27}$$

Clausius' original derivation of the second law is based on the statement that *heat will go from hot to cold by itself, but not vice versa.* We shall use this statement to learn more on thermodynamic temperature T. Since we declared T_H as the temperature of the hotter reservoir, heat should go from the reservoir at T_H to the reservoir at T_L. According to Fig. 4.4 the proper direction of heat transfer in accordance to Clausius' statement is for positive $\dot{Q}_H$, that is for $\dot{Q} > 0$, which implies $\dot{Q}_L < 0$. With $\dot{Q} > 0$ the inequality (4.27) holds for $\left(\frac{1}{T_L} - \frac{1}{T_H}\right) > 0$, which is fulfilled if (a) $T_H > T_L$, and (b) T_H and T_L have the same sign, i.e., T is either always positive or always negative. The discussion of friction in the next section will show that T must be positive.

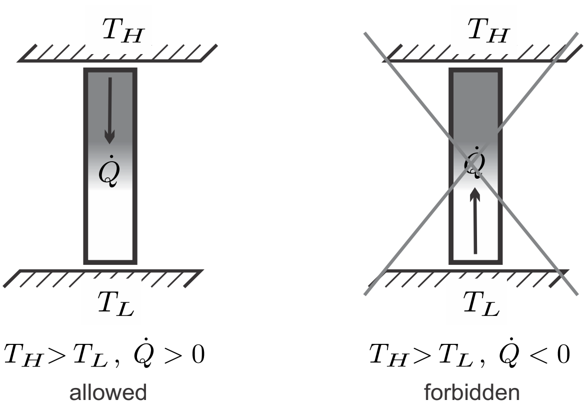

Fig. 4.5 Heat transfer between two reservoirs with $T_H > T_L$. Heat must go from warm to cold.

Figure 4.5 gives an illustration of the allowed process, where heat goes from hot to cold, and the forbidden process, where heat would go from cold to hot by itself.

4.9 Internal Friction

The sign of temperature follows from the observation that a stirred substance will come to rest due to friction with the container walls, and within the fluid. When coffee, or any other liquid, is stirred, it will spin a while after the spoon is removed. The motion will slow down because of internal friction, and finally the coffee will be at rest in the cup. The second law should describe this well-known behavior, which is observed in all viscous fluids.

With the fluid in motion, we have to account for the kinetic energy of the swirling, which must be computed by summation (i.e., integration), of the local kinetic energies $\frac{\rho(\overrightarrow{r})}{2}\mathcal{V}\left(\overrightarrow{r}\right)^2$ in all volume elements; see Fig. 4.6. The first and second law read

$$\frac{d\left(U+E_{kin}\right)}{dt}=\dot{Q}-\dot{W}\quad,\quad\frac{dS}{dt}-\sum\frac{\dot{Q}_k}{T_k}\geq 0\,. \tag{4.28}$$

We assume adiabatic systems ($\dot{Q}=0$) without any work exchange ($\dot{W}=0$, this implies constant volume), so that

$$\frac{d\left(U+E_{kin}\right)}{dt}=0\quad,\quad\frac{dS}{dt}\geq 0\,. \tag{4.29}$$

If we ignore local temperature differences within the stirred substance, we have with (4.9)

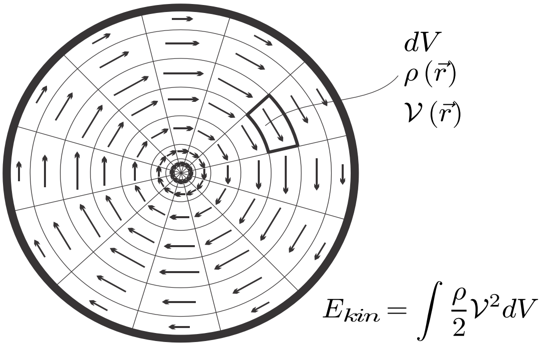

Fig. 4.6 The kinetic energy E_{kin} of a stirred fluid is the sum of the kinetic energies in all volume elements. Friction with the container wall, and within the fluid, will slow down the fluid until it comes to rest in the final equilibrium state.

$$\frac{dS}{dt} = \left(\frac{\partial S}{\partial U}\right)_V \frac{dU}{dt} = \frac{1}{T}\frac{dU}{dt} = -\frac{1}{T}\frac{dE_{kin}}{dt} \geq 0 \ . \tag{4.30}$$

Experience shows that over time the fluid slows down, hence the kinetic energy $E_{kin} = \int \frac{\rho}{2}\mathcal{V}^2 dV$ decreases over time, and will be zero in equilibrium, where the stirred substance comes to rest, $\mathcal{V} = 0$; this implies

$$\frac{dE_{kin}}{dt} \leqslant 0 \ . \tag{4.31}$$

The latter inequality is compatible with the 2nd law in the form (4.30) only if the thermodynamic temperature is non-negative, $T \geq 0$.

An equivalent experience is that work in transmission can be lost to friction, but not gained. Figure 4.7 shows the work and heat flows for a gearbox operating at constant temperature T, at steady state. The gearbox receives the work $-\left|\dot{W}_{in}\right|$, and delivers the work $\dot{W}_{out} > 0$. Moreover, the gearbox is in thermal contact with the environment from which it receives the heat $\dot{Q}$. The figure shows absolute values for work, the arrows indicate the direction of the work flows. The first law is straightforward to evaluate: Since the gear box operates at steady state, the energy supply must equal the energy loss. The statement of the first law can be read straight from the figure: Energy flow in (arrows pointing towards the gearbox) must be equal to energy flow out (arrows out of the gearbox),

$$\left|\dot{W}_{in}\right| + \dot{Q} = \dot{W}_{out} \ . \tag{4.32}$$

There is only a single heat flow contribution, therefore the second law becomes

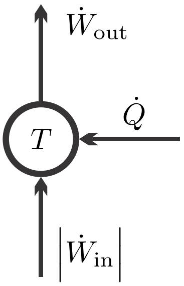

Fig. 4.7 Work and heat flow in a gearbox operating at constant temperature T. The heat is expected to be negative, $\dot{Q} < 0$.

$$-\frac{\dot{Q}}{T} = \frac{\left|\dot{W}_{in}\right| - \dot{W}_{out}}{T} = \dot{S}_{gen} \geq 0\ . \tag{4.33}$$

We consider it a general experience that some work is lost in the transmission through a gearbox, and that the box sheds heat into the environment,[2]

$$\dot{W}_{out} \leq \left|\dot{W}_{in}\right| \quad , \quad \dot{Q} < 0\ . \tag{4.34}$$

Comparison between the two last equations shows, again, that the thermodynamic temperature must not be negative, $T \geq 0$.

The lost work leaves the gearbox in form of heat $\left|\dot{Q}_{out}\right| = -\dot{Q} = \left|\dot{W}_{in}\right| - \dot{W}_{out} > 0$, which is transmitted into the environment. The reason for the loss is friction within the gearbox.

4.10 Newton's Law of Cooling

We return to the discussion of heat transfer. The inequality (4.27) requires that $\dot{Q}$ has the same sign as $\left(\frac{1}{T_L} - \frac{1}{T_H}\right)$, a requirement that is fulfilled for a heat transfer rate

$$\dot{Q} = \alpha A \left(T_H - T_L\right) \tag{4.35}$$

with a positive heat transfer coefficient $\alpha > 0$, and the heat exchange surface area A. This relation, which we already used in an example, is known as Newton's law of cooling, and is often used in heat transfer problems. The values of the positive coefficient α must be found from the detailed configuration and

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[2] This is tantamount to the statement that a system exchanging heat with a single reservoir cannot produce work (see Sec. 5.3 further below). Indeed, if the system would *receive* the heat $\dot{Q} > 0$, the first law would require $\dot{W}_{out} > \left|\dot{W}_{in}\right|$: more work would leave the system than enter, which means that the single incoming heat $\dot{Q}$ would be converted to work.

conditions in the heat transfer system. The surface area A appears due to the intuitive expectation that enlarging the transfer area leads to a proportional increase in the amount of heat transferred.

Heat transfer was introduced as energy transfer due to temperature difference with heat going from hot to cold, Newton laws of cooling states that as a result of the temperature difference one will observe a response, namely the heat flux.

The procedure to derive Newton's law of cooling can be described as follows: The entropy generation rate (4.27) is interpreted as the product of a thermodynamic force—here, the temperature difference $(T_H - T_L)$—and a corresponding flux—here, the heat flux $\dot{Q}$. To ensure positivity of the entropy generation rate, the flux must be proportional to the force, with a positive factor αA that must be measured. The same strategy can be used for other force-flux pairs.

With Newton's law of cooling it is easy to see that heat transfer over finite temperature differences is an irreversible process. Indeed, the second law (4.27) gives with (4.35)

$$\dot{S}_{gen} = \dot{Q}\left(\frac{1}{T_L} - \frac{1}{T_H}\right) = \alpha A \frac{(T_H - T_L)^2}{T_L T_H} > 0 \ . \tag{4.36}$$

Only when the temperature difference is infinitesimal, i.e., $T_H = T_L + dT$, entropy generation can be ignored, and heat transfer can be considered as a reversible process. This can be seen as follows: For infinitesimal dT the entropy generation rate becomes $\dot{S}_{gen} = \alpha A \left(\frac{dT}{T_L}\right)^2$. Since quadratic terms in infinitesimal differences can be ignored, this implies $\dot{S}_{gen} = 0 \ (dT \to 0)$. In this case, to have a finite amount of heat transferred, the heat exchange area A must go to infinity.

4.11 Zeroth Law and Second Law

While above we considered heat transfer between reservoirs, the conclusion is valid for heat conduction between arbitrary systems: As long as the systems are in thermal contact through heat conductors, and their temperatures are different, there will be heat transfer between the systems. Only when the temperatures of the systems are equal, heat transfer will cease. This is the case of thermal equilibrium, where no change in time occurs anymore. This includes that the temperature of an isolated body in thermal equilibrium will be homogeneous, where equilibration occurs through heat transfer within the system.

The zeroth law states: In equilibrium systems in thermal contact assume the same temperature. Thus, the zeroth law of thermodynamics might appear as a special case of the second law. It stands in its own right, however, since it *defines* temperature as a measurable quantity.

4.12 Example: Equilibration of Temperature

We return to the problem considered in Sec. 3.12, the equilibration of temperature between two bodies A and B, with initial temperatures $\bar{T}_A$ and $\bar{T}_B$. The first law alone was not sufficient to find the final common temperature, which will now be obtained from the second law. The compound system $A+B$ is adiabatic to the outside, so that the second law becomes

$$\frac{dS}{dt} = \frac{d\left(S_A + S_B\right)}{dt} \geq 0 \; .$$

Thus the total entropy $S = S_A + S_B$ of the system will grow in time until it will assume its maximum in equilibrium, when no further changes occur.

For the simple solids under consideration, by (4.14) the entropy is $S = mc \ln \frac{T}{T_0}$, so that

$$S = S_A + S_B = m_A c_A \ln \frac{T_A}{T_0} + m_B c_B \ln \frac{T_B}{T_0} \; .$$

The first law relates the actual temperatures T_A and T_B of the two bodies and their initial temperatures $\bar{T}_A$, $\bar{T}_B$ through (3.26). With this, the entropy of the system becomes a function of T_B only,

$$S = m_A c_A \ln \left(\frac{\bar{T}_A}{T_0} + \frac{m_B c_B}{m_A c_A} \frac{\bar{T}_B - T_B}{T_0} \right) + m_B c_B \ln \frac{T_B}{T_0} \; .$$

Since the entropy of the compound system $A+B$ can only grow, in equilibrium the entropy assumes the largest possible value, which is obtained from the condition $\frac{dS}{dT_B} = 0$. The evaluation, left as an exercise for the reader, gives the expected result for the common equilibrium temperature,

$$T_B = T_A = T = \frac{m_A c_A \bar{T}_A + m_B c_B \bar{T}_B}{m_A c_A + m_B c_B} \; .$$

4.13 Example: Uncontrolled Expansion of a Gas

We consider the entropy change for the uncontrolled expansion of an ideal gas in Sec. 3.13, for which the first law gave $T_1 = T_2$. The second law for this adiabatic process simply reads

$$\frac{dS}{dt} = \dot{S}_{gen} \geq 0.$$

Integration over the process duration yields

$$S_2 - S_1 = \int_{t_1}^{t_2} \dot{S}_{gen} dt = S_{gen} \geq 0 \; .$$

The total change of entropy follows from the ideal gas entropy (with constant specific heat), Eq. (4.19) as

$$S_2 - S_1 = m\left(s_2 - s_1\right) = mR\ln\frac{V_2}{V_1} = mR\ln\frac{p_1}{p_2} \geq 0 \; .$$

Since in this process the temperature of the ideal gas remains unchanged, the growth of entropy is only attributed to the growth in volume: by filling the larger volume V_2, the gas assumes a state of larger entropy. Since the container is adiabatic, there is no flux of entropy over the boundary (i.e., $\sum \frac{\dot{Q}_k}{T_k} = 0$), and all entropy generated stays within the system, $S_{gen} = S_2 - S_1$.

4.14 What Is Entropy?

The arguments that gave us the second law and entropy as a property centered around the trend to equilibrium observed in any system left to itself (isolated system). Based on the derivation, the question *What is entropy?* can be answered simply by saying *It's a quantity that arises when one constructs an inequality that describes the trend to equilibrium.* Can there be a deeper understanding of entropy?

Before we try to answer, we look at internal energy: When the first law of thermodynamics was found, the concept of internal energy was new, and it was difficult to understand what it might describe. At that time, the atomic structure of matter was not known, and internal energy could not be interpreted—it appeared because it served well to describe the phenomena. Today we know more, and we understand internal energy as the kinetic and potential energies of atoms and molecules on the microscopic level. Thus, while the concept of internal energy arose from the desire to describe phenomena, today it is relatively easy to understand, because it has a macroscopic analogue in mechanics.

Entropy also came into play to describe the phenomena, but it is a new quantity, without a mechanical analogue. A deeper understanding of entropy can be gained, as for internal energy, from considerations on the atomic scale. Within the framework of his *Kinetic Theory of Gases*, Ludwig Boltzmann (1844-1905) found a microscopic interpretation of entropy, where entropy is related to concepts of probability. A not too precise description of this interpretation follows below.

Macroscopically, a state is described by only a few macroscopic properties, e.g., temperature, pressure, volume. Microscopically, a state is described through the location and momentum of all atoms within the system. The microscopic state is constantly changing due to the microscopic motion of the atoms, and there are many microscopic states that describe the same macroscopic state. If we denote the total number of all microscopic states that describe the same macroscopic state by Ω, then the entropy of the macroscopic state according to Boltzmann is

$$S = k_B \ln \Omega \, . \tag{4.37}$$

The constant $k_B = \bar{R}/A = 1.3804 \times 10^{-23} \frac{\mathrm{J}}{\mathrm{K}}$ is the Boltzmann constant, which can be interpreted as the gas constant per particle.

The growth of entropy in an isolated system, $\frac{dS}{dt} \geq 0$, thus means that the system shifts to macrostates which have larger numbers of microscopic realizations. Equilibrium states have particularly large numbers of realizations, and this is why they are observed.

To make the ideas somewhat clearer, we consider the expansion of a gas when a barrier is removed, see Secs. 3.13, 4.13. This is a particularly simple case, where the internal energy, and thus the distribution of energy over the particles, does not change. Hence, we can ignore the distribution of thermal energy over the particles, and the exchange of energy between them.

We assume a system of N gas particles in a volume V. The volume of a single particle is v_0, and in order to be able to compute the number Ω, we "quantize" the accessible volume V into $n = V/v_0$ boxes that each can accommodate just one particle. Note that in a gas, where the distance between individual particles is relatively large, most boxes are empty. Due to their thermal energy, the atoms move from box to box. The number of microstates is simply given by the number of realizations of a state with N filled boxes and $(n - N)$ empty boxes, which is

$$\Omega \left(N, V \right) = \frac{n!}{N! \left(n - N \right)!} \, . \tag{4.38}$$

By means of Stirling's formula $\ln x! = x \ln x - x$ (for $x \gg 1$) the entropy (4.37) for this state becomes

$$S \left(N, V \right) = k_B \left[-N \ln \frac{N}{n} - \left(n - N \right) \ln \left(1 - \frac{N}{n} \right) \right] \, . \tag{4.39}$$

Now we can compute the change of entropy with volume. For this, we consider the same N particles in two different volumes, $V_1 = n_1 v_0$ and $V_2 = n_2 v_0$. The entropy difference $S_2 - S_1 = S\left(N, V_2\right) - S\left(N, V_1\right)$ between the two states can be written as

$$\begin{aligned} S_2 - S_1 = k_B \Bigg[& N \ln \frac{n_2}{n_1} + n_1 \ln \left(1 - \frac{N}{n_1} \right) \\ & - n_2 \ln \left(1 - \frac{N}{n_2} \right) + N \ln \frac{\left(1 - \frac{N}{n_2} \right)}{\left(1 - \frac{N}{n_1} \right)} \Bigg] \, . \end{aligned} \tag{4.40}$$

In an ideal gas the number of possible positions n is much bigger than the number of particles N, that is $\frac{N}{n_1} \ll 1, \frac{N}{n_2} \ll 1$. Taylor expansion yields the entropy difference to leading order as

$$S_2 - S_1 = k_B N \ln \frac{n_2}{n_1} = mR \ln \frac{V_2}{V_1} \ , \tag{4.41}$$

where we reintroduced volume ($V_{1,2} = n_{1,2} v_0$), and introduced the mass as $m = M\,N/A$; $R = \bar{R}/M$ is the gas constant. This is just the change of entropy computed in Sec. 4.13.

It is instructive to compare the number of realizations for the two cases, for which we find

$$\frac{\Omega_2}{\Omega_1} = \exp \frac{S_2 - S_1}{k} = \exp \left(N \ln \frac{V_2}{V_1} \right) = \left(\frac{V_2}{V_1} \right)^N \ . \tag{4.42}$$

For a macroscopic amount of gas, the particle number N is extremely large (order of magnitude $\sim 10^{23}$), so that already for a small difference in volume the ratio of microscopic realization numbers is enormous. For instance for $V_2 = 2V_1$, we find $\frac{\Omega_2}{\Omega_1} = 2^N$.

Microscopic states change constantly due to travel of, and collisions between, particles. Each of the Ω microstates compatible with the given macrostate is observed with the same probability, $1/\Omega$. The Ω_1 microstates in which the gas is confined in the volume V_1 are included in the Ω_2 microstates in which the gas is confined in the larger volume V_2. Thus, after removal of the barrier, there is a finite, but extremely small probability of $P = \frac{\Omega_1}{\Omega_2} = \left(\frac{V_1}{V_2} \right)^N$ to find all gas particles in the initial volume V_1. This probability is so small that the expected waiting time for observing a return into the original volume exceeds the lifetime of the universe by many orders of magnitude. If we do not want to wait that long for the return to initial state, we have to push the gas back into the initial volume, which requires work.

In generalization of the above, we can conclude that it is quite unlikely that a portion V_ν of the volume is void of particles. The corresponding probability is $P_\nu = \left(\frac{V - V_\nu}{V} \right)^N$. The average volume available for one particle is $\bar{V} = \frac{V}{N}$, and when $V_\nu = \nu \bar{V}$ we find, for the large particle numbers in an macroscopic amount of gas, $P_\nu = \left(1 - \frac{\nu}{N} \right)^N \simeq e^{-\nu}$. Thus, as long as V_ν is bigger than the average volume for a single particle, so that $\nu > 1$, the probability for a void is very small. Moreover, inhomogeneous distributions are rather unlikely, since the number of homogeneous distributions is far larger than the number of strongly inhomogeneous distributions. This is why we observe homogeneous distributions in equilibrium.

Figure 4.8 gives an illustration of microstates for a rather small system. The system of $N = 9$ particles with $n = 81$ boxes allows for $\Omega = \frac{81!}{9!(81-9)!} = 2.61 \times 10^{11}$ microstates, three of which are shown in the figure. Microstate A is one of the $\Omega_L = \frac{27!}{9!(27-9)!} = 4.69 \times 10^6$ microstates in which the gas in confined to the left third of the system. Microstates B and C are more homogeneous distributions.

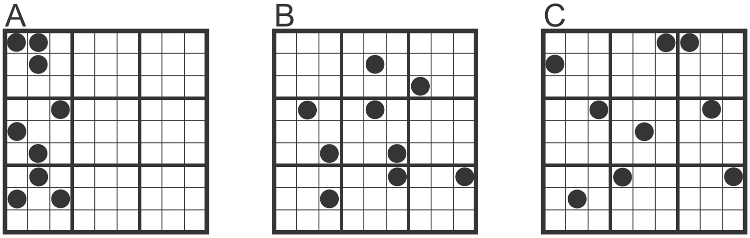

Fig. 4.8 A system of 9 particles with 81 accessible positions in three different microstates *A*, *B*, *C*

4.15 Entropy and Disorder

Often it is said that entropy is a measure for disorder, where disorder has a higher entropy. This can be related to the above discussion by means of the following analogy: The ordered state of an office is the state where all papers, folders, books and pens are in their designated shelf space. Thus, they are confined to a relatively small initial volume of the shelf, V_1. When work is done in the office, all these papers, folders, books and pens are removed from their initial location, and, after they are used, are dropped somewhere in the office—now they are only confined to the large volume of the office, V_2. The actions of the person working in the office constantly change the microstate of the office (the precise location of that pen ... where is it now?), in analogy to thermal motion.

At the end of the day, the office looks like a mess and needs work to clean up. Note, however, that the final state of the office—which appears to be so disorderly—is just *one* accessible microstate, and therefore it has the same probability as the fully ordered state, where each book and folder is at its designated place on the shelf. A single microstate, e.g., a particular distribution of office material over the office in the evening, has no entropy. Entropy is a macroscopic property that counts the number of all possible microstates, e.g., all possible distributions of office material.

A macroscopic state which puts strong restrictions on the elements has a low entropy, e.g., when all office material is in shelves behind locked doors. When the restrictions are removed—the doors are unlocked—the number of possible distributions grows, and so does entropy. Thermal motion leads to a constant change of the distribution within the inherent restrictions.

To our eye more restricted macroscopic states—all gas particles only in a small part of the container, or all office material behind closed doors—appear more orderly, while less restricted states generally appear more disorderly. In this sense one can say that entropy is a measure for disorder.

In the office, every evening the disordered state differs from that of the previous day. Over time, one faces a multitude of disordered states, that is the disordered office has many realizations, and a large entropy. In the end, this makes cleaning up cumbersome, and time consuming.

Our discussion focussed on spatial distributions where the notion of order is well-aligned with our experience. The thermal contribution to entropy is related to the distribution of microscopic energy e_m over the particles, where e_m is the microscopic energy per particle. In *Statistical Thermodynamics* one finds that in equilibrium states the distribution of microscopic energies between particles is exponential, $A \exp\left[-\frac{e_m}{kT}\right]$. The factor A must be chosen such that the sum over all particles gives the internal energy, $U = \sum_m A e_m \exp\left[-\frac{e_m}{k_B T}\right]$. One might say that the exponential itself is an orderly function, so that the equilibrium states are less disordered than non-equilibrium states. Moreover, for lower temperatures the exponential is more narrow, the microscopic particle energies are confined to lower values, and one might say that low temperature equilibrium states are more orderly than high temperature equilibria. And indeed, we find that entropy grows with temperature, that is colder systems have lower entropies.

4.16 Entropy and Life

The second law states that systems left to themselves tend to disorder, in the non-trivial sense discussed above. To leave a system to itself, it must be isolated from its surroundings, so that no transport of mass and energy over the system boundaries occurs. For such a system the second law reads $\frac{dS}{dt} \geq 0$, entropy—disorder—must increase. A system which is not isolated can have decreasing entropy. Indeed, for a closed system the second law reads $\frac{dS}{dt} - \sum \frac{\dot{Q}_k}{T_k} \geq 0$; thus, by suitable manipulation of the system, in particular cooling ($\dot{Q}_k < 0$), its entropy can decrease, more ordered states are possible.

Earth itself is not isolated, since it receives an abundance of high temperature energy from the sun in form of radiation (sun surface temperature $T_S \simeq 5700\,\mathrm{K}$). At the same time Earth emits low temperature energy, also in form of radiation (Earth surface temperature $T_E \simeq 300\,\mathrm{K}$). This exchange of energy with Earth's surrounding allows decreasing entropy locally on the planet. When we assume that the amount of heat received and emitted by radiation is the same ($\left|\dot{Q}\right|$), the second law for Earth reads $\frac{dS}{dt} \geq \left|\dot{Q}\right| \left(\frac{1}{T_S} - \frac{1}{T_E}\right)$. Since $T_S > T_E$, the left hand side is negative, Earth's entropy may, but must not, decrease.

If entropy is decreasing within a system (which cannot be isolated!), entropy must be growing somewhere else. When a sufficient portion of the surroundings are included in the system, entropy must grow. The entropy in the universe, which is a rather large isolated system, is increasing. The processes in the sun create entropy locally, in the sun.

Life, most importantly, is fed by the sun. Just think of the human body: we grow, we learn, and thus keep disorder within the confines of our body rather small. As humans are open systems, we maintain a low entropy level by exchange of mass and energy with our surroundings. Within the larger system around us, entropy grows, but within the smaller boundaries of our bodies (and minds!), entropy decreases, or is at least maintained at the same level.

The sun is the source of life, since it provides the energy we need to lower entropy in our open system Earth, and in our open system human body. Evolution, as an increase of order, does not contradict the second law.

4.17 The Entropy Flux Revisited

When we discussed the possible form of the entropy flux $\dot{\Psi}$ in Sec. 4.3, we introduced two coefficients β, γ but we soon set them to $\beta = 1/T$ and $\gamma = 0$ in order to simplify the proceedings. In this section, we run briefly through the proper line of arguments that show that γ must be a constant, which can be set to zero. The argument also shows that β must depend only on temperature, must grow inversely to temperature, and must be positive. Thus β behaves like inverse thermodynamic temperature, which agrees with our statements above.

For the argument we split the inhomogeneous system under consideration into a large number of small subsystems, each with their individual properties, see Fig. 4.3. With the entropy flux $\dot{\Psi} = \beta\dot{Q} - \gamma\dot{W}$ we find the second law for non-equilibrium systems from summing over subsystems as

$$\frac{dS^{(\gamma)}}{dt} + \sum \gamma_k \dot{W}_k - \sum \beta_k \dot{Q}_k = \dot{S}_{gen} \geq 0 \,, \tag{4.43}$$

where $S^{(\gamma)}$ is the entropy for this choice of flux. As before, $\dot{Q}_k$, $\dot{W}_k$ denote the exchange of heat and work with the surroundings of the system, and β_k, γ_k are the corresponding values of the unknown coefficients in the sub-systems at the system boundaries. All internal exchange of heat and work between the subsystems must be such that entropy is generated. The corresponding terms are absorbed in the entropy generation rate $\dot{S}_{gen}$. The first law for the system is given in (4.23).

We consider the above form (4.43) of the second law for a heat conductor. For steady state heat transfer without any work exchange between a hot reservoir (H) and a cold reservoir (L) through the heat conductor, the above reduces to

$$-\beta_H \dot{Q}_H - \beta_L \dot{Q}_L = \dot{S}_{gen} \geq 0 \,. \tag{4.44}$$

Here, β_H and β_L are the values of β at the hot and cold sides of the conductor, respectively. The first law gives $\dot{Q}_H = -\dot{Q}_L = \dot{Q}$ so that

$$\left(\beta_L - \beta_H\right) \dot{Q} = \dot{S}_{gen} \geq 0 \,. \tag{4.45}$$

Since heat must go from hot to cold, the heat must be positive, $\dot{Q} > 0$, which requires $(\beta_L - \beta_H) > 0$. Thus, the coefficient β must be smaller for the part of the system which is in contact with the hotter reservoir. This must be so irrespective of the values of any other properties at the system boundaries (L, H). Therefore β must depend on temperature *only*.

It follows that β must be a decreasing function of temperature alone, if temperature of hotter states is defined to be higher. The left part of Fig. 4.9 shows a schematic of the heat transfer process.

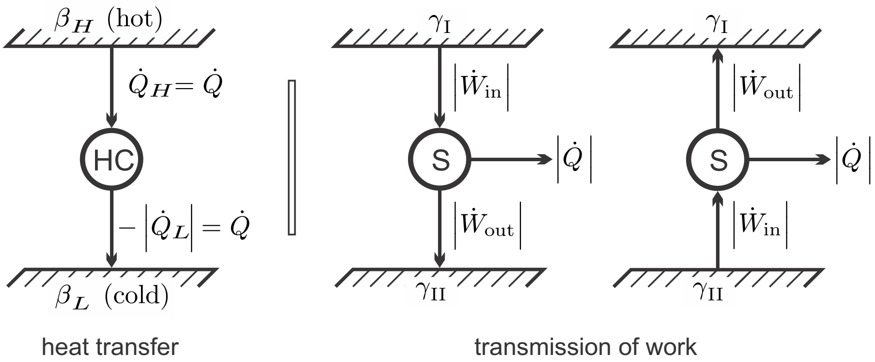

Fig. 4.9 Heat transfer through a heat conductor *HC* (left) and transmission of work through a steady state system *S* (right)

We proceed with the discussion of the coefficient γ. For this, we turn our attention to the transmission of work. The right part of Fig. 4.9 shows two "reservoirs" characterized by different values γ_{I}, γ_{II} between which work is transmitted by a steady state system S. The direction of work transfer is not restricted: by means of gears and levers work can be transmitted from low to high force and vice versa, and from low to high velocity and vice versa. Therefore, transmission might occur from I to II, and as well from II to I. Accordingly, there is no obvious interpretation of the coefficient γ.

Friction might occur in the transmission. Thus, in the transmission process we expect some work lost to frictional heating, therefore $\left|\dot{W}_{out}\right| \leq \left|\dot{W}_{in}\right|$. In order to keep the transmission system at constant temperature, some heat must be removed. Work and heat for both cases are indicated in the figure, the arrows indicate the direction of transfer.

The first law for both transmission processes reads (steady state, $\frac{dU}{dt} = 0$)

$$0 = -\left|\dot{Q}\right| - \left|\dot{W}_{out}\right| + \left|\dot{W}_{in}\right| \ , \tag{4.46}$$

where the signs account for the direction of the fluxes. Since work loss in transmission means $\left|\dot{W}_{out}\right| \leq \left|\dot{W}_{in}\right|$, this implies that heat must leave the system, $\dot{Q} = -\left|\dot{Q}\right| \leq 0$.

Due to the different direction of work in the two processes considered, the second law (4.43) gives different conditions for both situations,

$$-\gamma_{\mathrm{I}}\left|\dot{W}_{in}\right| + \gamma_{\mathrm{II}}\left|\dot{W}_{out}\right| + \beta\left|\dot{Q}\right| \geq 0\ ,\quad \gamma_{\mathrm{I}}\left|\dot{W}_{out}\right| - \gamma_{\mathrm{II}}\left|\dot{W}_{in}\right| + \beta\left|\dot{Q}\right| \geq 0\ , \tag{4.47}$$

where, as we have just seen, β is a measure for the temperature of the transmission system. Elimination of the heat between first and second laws gives two inequalities,

$$(\gamma_{\mathrm{II}} - \beta)\left|\dot{W}_{out}\right| - (\gamma_{\mathrm{I}} - \beta)\left|\dot{W}_{in}\right| \geq 0\ ,\ (\gamma_{\mathrm{I}} - \beta)\left|\dot{W}_{out}\right| - (\gamma_{\mathrm{II}} - \beta)\left|\dot{W}_{in}\right| \geq 0, \tag{4.48}$$

or, after some reshuffling,

$$(\beta - \gamma_{\mathrm{II}})\frac{\left|\dot{W}_{out}\right|}{\left|\dot{W}_{in}\right|} \leq (\beta - \gamma_{\mathrm{I}}) \quad , \quad (\beta - \gamma_{\mathrm{I}})\frac{\left|\dot{W}_{out}\right|}{\left|\dot{W}_{in}\right|} \leq (\beta - \gamma_{\mathrm{II}})\ . \tag{4.49}$$

Combining the two equations gives the two inequalities

$$(\beta - \gamma_{\mathrm{I}})\left(\frac{\left|\dot{W}_{out}\right|}{\left|\dot{W}_{in}\right|}\right)^2 \leq (\beta - \gamma_{\mathrm{I}}) \quad , \quad (\beta - \gamma_{\mathrm{II}})\left(\frac{\left|\dot{W}_{out}\right|}{\left|\dot{W}_{in}\right|}\right)^2 \leq (\beta - \gamma_{\mathrm{II}})\ . \tag{4.50}$$

From the latter follows, since $0 \leq \frac{|\dot{W}_{out}|}{|\dot{W}_{in}|} \leq 1$, that $(\beta - \gamma)$ must be non-negative.

Both inequalities (4.49) must hold for arbitrary transmission systems, that is for all $0 \leq \frac{|\dot{W}_{out}|}{|\dot{W}_{in}|} \leq 1$, and all β. For a reversible transmission, where $\frac{|\dot{W}_{out}|}{|\dot{W}_{in}|} = 1$, both inequalities (4.49) can only hold for $\gamma_{\mathrm{I}} = \gamma_{\mathrm{II}}$. Accordingly, $\gamma_{\mathrm{I}} = \gamma_{\mathrm{II}} = \gamma$ must be a constant, and $(\beta - \gamma) \geq 0$ for all β.

With γ as a constant, the entropy balance (4.43) becomes

$$\frac{dS^{(\gamma)}}{dt} + \gamma\dot{W} - \sum \beta_k \dot{Q}_k = \dot{S}_{gen} \geq 0\ . \tag{4.51}$$

The energy balance $\dot{W} = \sum \dot{Q}_k - \frac{dE}{dt}$ allows to eliminate work,

$$\frac{d\left(S^{(\gamma)} - \gamma E\right)}{dt} - \sum\left(\beta_k - \gamma\right)\dot{Q}_k = \dot{S}_{gen} \geq 0\ . \tag{4.52}$$

With $S = S^{(\gamma)} - \gamma E$ as the standard entropy, and $T = 1/(\beta - \gamma)$ as the positive thermodynamic temperature, we find the second law in the form (4.24). This is equivalent to setting $\gamma = 0$, and $\beta = 1/T$ as was done in Sec. 4.4.

Problems

4.1. Isothermal Stirring of Mercury

2 litre of mercury confined in a container in thermal contact to an environment at 15 °C are stirred with a 200 W stirrer. How much entropy is created in 20 minutes of stirring? Does the entropy of the mercury change? What happens to the entropy created?

4.2. Adiabatic Stirring of Mercury

2 litre of mercury confined in an isolated container are stirred with a 200 W stirrer. When the mercury was at 15 °C initially, what is its temperature after 20 minutes of stirring? How much entropy is created in the process? What happens to the entropy created?

4.3. Kneading of Pizza Dough

2 kg of dough ($c = 2.73 \frac{\mathrm{kJ}}{\mathrm{kg\,K}}$) confined in a container are kneaded with a 350 W kitchen mixer.

1. The container is in thermal contact to an environment at 25 °C so that the temperature of the dough is 25 °C at all times. How much entropy is created in 10 minutes of kneading?
2. The container is thermally isolated. When the dough was at 25 °C initially, how long does it take until the temperature is 40 °C? How much entropy is created in the process?
3. Both processes are irreversible, hence entropy is created. Explain where the produced entropy goes.

4.4. Stirring of Petroleum

4 litre of petroleum ($\rho = 640 \frac{\mathrm{kg}}{\mathrm{m}^3}$, $c_p = 2.0 \frac{\mathrm{kJ}}{\mathrm{kg\,K}}$) confined in an isolated rigid container are stirred by an electric motor which consumes 50 W of electrical power.

1. How long does it take until the temperature of the petroleum is raised by 5 °C?
2. What is the relation between entropy generation and power? Is the process reversible or irreversible?

4.5. Industrial Stirrer

During manufacture, 2 tons of polyethylene (incompressible liquid, specific heat $c = 2.9308 \frac{\mathrm{kJ}}{\mathrm{kg\,K}}$) are stirred in a well-insulated container for 20 minutes. It is observed that the temperature rises from 42 °C to 49 °C. Ignoring kinetic and potential energies, determine the power demand of the stirrer, and the entropy generated during the process.

4.6. A Brick Falls

A 2 t brick cube falls to the ground on a planet without atmosphere. The gravitational acceleration is $1\frac{\mathrm{m}}{\mathrm{s}^2}$. The cube crashes on the ground and comes to rest. From what height must the cube fall to increase its temperature by 10 K? When the brick's initial temperature was 200 K, how much entropy is created in the process? How much work could be obtained in a reversible process? Brick: $\rho = 1922\frac{\mathrm{kg}}{\mathrm{m}^3}$, $c = 0.79\frac{\mathrm{kJ}}{\mathrm{kg\,K}}$

4.7. A Bad Accident

A 2t truck running at a speed of 120 km/ h crashes against a concrete wall and comes to rest. Assume that the truck is made of steel ($\rho = 7830\frac{\mathrm{kg}}{\mathrm{m}^3}$, $c = 0.5\frac{\mathrm{kJ}}{\mathrm{kg\,K}}$), and that all energy stays in the truck.

1. By what amount will the average temperature of the truck change?
2. How much entropy is created in the process? Assume initial temperature is $T_0 = 20\,{}^\circ\mathrm{C}$.
3. How much work could have been obtained in a reversible process, e.g., by electromagnetic brakes that charge a battery? Compare the possible work to $T_0 S_{gen}$.

4.8. Dissipation of Kinetic Energy

In Sec. 4.9 it was shown that in an isolated system kinetic energy will vanish in equilibrium. Repeat the proof for a non-adiabatic system.

4.9. Tank and Contents

A well-insulated steel tank of mass 10 kg contains 5 litre of liquid water. Initially, the temperature of the tank is 7 °C, and the temperature of the water is 90 °C. Specific heats: $c_{steel} = 0.5\frac{\mathrm{kJ}}{\mathrm{kg\,K}}$, $c_{water} = 4.18\frac{\mathrm{kJ}}{\mathrm{kg\,K}}$

1. What is the temperature of the system after equilibrium is established?
2. Compute the change of entropy of the tank.
3. Compute the change of entropy of the water.
4. How much entropy is created in the process? Is the process reversible or irreversible?

4.10. Property Change in Argon

The state of argon (ideal gas with constant specific heats) is changed by heating and compression from initial state $p_1 = 1\,\mathrm{bar}$, $T_1 = 230\,\mathrm{K}$ to the final state $p_2 = 20\,\mathrm{bar}$, $T_2 = 400\,\mathrm{K}$. Compute the change of internal energy and the change of entropy of the gas. Do you have enough information to compute the heat and work exchanged? Why not?

4.11. Work and Heat

Krypton (Kr) gas at $T_1 = 230\,{}^\circ\mathrm{C}$ is confined in a piston-cylinder system. The gas undergoes a reversible process where the pressure changes according to the relation $p = p_1 (V_1/V)^2$. The initial and final volumes are $V_1 = 0.2\,\mathrm{m}^3$ and $V_2 = 0.1\,\mathrm{m}^3$ and the initial pressure is $p_1 = 4\,\mathrm{bar}$.

As all monatomic gases, krypton behaves as an ideal gas with constant specific heat; its molar mass is $M = 83.8\frac{\mathrm{kg}}{\mathrm{kmol}}$. Determine:

1. The mass of Kr in the system.
2. Pressure p_2 and temperature T_2 at the end of the process.
3. The total work for the process.
4. The total heat exchange.
5. The change of entropy of the gas.

4.12. Irreversible Expansion of Xenon

Xenon (ideal gas with constant specific heats) is confined in one half of a 2.5 litre container. The other half of the container is evacuated, and the container is well-insulated. When the partition is removed, the gas expands irreversibly to fill the whole container. Initially, the xenon is at $p_1 = 20\,\text{bar}$, $T_1 = 400\,\text{K}$. Compute the final state p_2, T_2 and the entropy generated.

4.13. Irreversible Expansion of Neon

Neon (ideal gas with constant specific heats) is confined in a 1 litre gas container at $p_1 = 13\,\text{bar}$, $T_1 = 500\,\text{K}$. This container is enclosed in an evacuated rigid container of unknown volume, which is well-insulated. The inner container becomes defect, and the neon expands irreversibly to fill the accessible volume. The final pressure is measured as 4 bar. From the first and second law determine the final temperature T_2, the volume of the bigger container, and the entropy generated.

4.14. Ideal Gas with Non-constant Specific Heat

We go back to problem 3.12, where you made a table of values for $c_v(T)$, $c_p(T)$, $u(T)$ and $h(T)$ for air, when the specific heat at constant volume is $c_v(T) = \left(0.695 + \frac{0.0598T}{1000\,\text{K}}\right)\frac{\text{kJ}}{\text{kg}\,\text{K}}$.

1. To your table, add a column for the entropy at standard pressure p_0, defined as $s^0(T) = \int_{T_0}^{T} \frac{c_p(T')}{T'} dT + s_0$ for temperatures in the range $(300\,\text{K}, 900\,\text{K})$. As reference value chose $s^0(300\,\text{K}) = 7.14\frac{\text{kJ}}{\text{kg}\,\text{K}}$.
2. 3 kg of air are heated in a reversible isochoric process (constant volume) from 320 K, 2 bar to 800 K. By means of your table, determine the work W_{12}, the heat supply Q_{12}, and the change in entropy, $S_2 - S_1$.
3. Redo the calculation of 2. under the assumption that the specific heat can be approximated by its value at 300 K (so that it is constant). Determine the relative errors for heat, work and entropy difference.

4.15. Equilibrium State I

N blocks of different metals with masses m_i, specific heats c_i and temperatures T_i are enclosed in an adiabatic rigid chamber. All blocks are brought into thermal contact. Use the first and second law to show that in equilibrium all blocks must have the same temperature.

Hint: In equilibrium entropy must be a maximum. Since energy is conserved, entropy must be maximized under the constraint of given energy. The most elegant way to solve the problem is using the method of Lagrange multipliers to take care of the constraint.

4.16. Equilibrium State II

An insulated container holds the mass $m_0 = \int \rho dV$ of an ideal gas, and the overall energy is fixed at $E_0 = \int \rho \left(u\left(T\right) + \frac{1}{2}\mathcal{V}^2 + gz \right) dV$. Note that in general density ρ, temperature T and velocity $\mathcal{V}$ depend on location $\overrightarrow{r}$. Show that in equilibrium temperature is homogeneous, density follows the barometric law, and velocity vanishes.

Hint: Here you have to maximize total entropy $S = \int \rho s\left(T, \rho\right) dV$ under constraints of given mass and energy. Use Lagrange multipliers and Euler's equation of variational calculus.

4.17. Equilibrium State III

An insulated room contains a rigid shelf on which rests a metal ball (mass m, specific heat c, initial temperature T). The shelf is at height H above the floor. By using first and second law, answer the following questions: Is the system in a thermodynamic equilibrium state, and if so, why? If not, what is the system's thermodynamic equilibrium state, and why? Does your answer depend on whether the room is evacuated, or filled with air? If you find the system is not in thermodynamic equilibrium, why do we find it in the unstable configuration?