

Thermodynamics and Kinetic Theory

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1 What is thermodynamics?

Thermodynamics is mainly concerned with the transformations of heat into mechanical work and the opposite transformations of mechanical work into heat.

But what are work and heat?

While *work* is a relatively well-understood concept from Newtonian mechanics and classical electrodynamics, it is less obvious what *heat* really is. For a long time, scientists believed that heat was some sort of fluid whose total amount was invariable, and heating of a body was transfer of this fluid from one body to another. Only in the mid-1800s, when the theory of thermodynamics was developed, did it crystallize that heat is a form of energy, and that heat and mechanical work are equivalent.

Thermodynamics is a phenomenological theory. This means that it formulates a few basic postulates based on experimental evidence and derives conclusions from these postulates. It does not make (or need!) any assumptions about the microscopic mechanisms underlying the phenomena observed.

Having an insight into such microscopic mechanisms, on the other hand, is often very useful and also more satisfying, since pure thermodynamics can be rather abstract. The kinetic theory of gases explains the equivalence of heat and mechanical work by reducing all thermal phenomena to the disordered Newtonian motion of large numbers of atoms and molecules. More generally, the fundamental laws of thermodynamics can be derived very satisfactorily from the theory of statistical mechanics, which also accounts for quantum mechanical effects.

Some historical context and milestones of thermodynamics:

1760–1840 Industrial revolution: transition from hand production to machines

1710–1770 Steam engines (Watt, ...)

1780s Electric batteries (Galvani, Volta)

1800–1850 Steam and electric locomotives, railways

> 1850 Age of oil: use of refined petroleum as fuel and in machines

1850–1900 Internal combustion engines (Otto, Diesel, ...)

1886 Cars (Benz)

1687 Newton's Principia

1824 Second law of thermodynamics: limitations on converting heat into mechanical work (Carnot)

1840s First law of thermodynamics: equivalence of heat and work, conservation of energy (Joule, Mayer)

1850s Definition of entropy (Rankine, Clausius)

1870s Kinetic theory and statistical mechanics (Maxwell, Boltzmann, Gibbs)

1912 Third law of thermodynamics: entropy at zero temperature, needs quantum mechanics (Nernst)

2 Thermodynamic systems

2.1 Thermodynamic variables

Typical systems we consider in thermodynamics are

- a block of iron,
- a bucket of water,
- a balloon filled with Helium gas.

These systems have two important aspects in common. They

- (i) occupy a volume much larger than the extension of their constituent particles (atoms and molecules),
- (ii) contain a large number of these constituent particles.

Systems with qualities (i) and (ii) are called *macroscopic*. This is in contrast to microscopic systems, which are typically tiny and may contain only a few particles.

In each example system, we could try to describe the physics by solving Newton's equations of motions for each of the N particles in the system. Complete information then requires to determine the position $\mathbf{x}_i = (x_i, y_i, z_i)$ and velocity $\mathbf{v}_i = (v_{x,i}, v_{y,i}, v_{z,i})$ for each particle, $i = 1, \dots, N$, at each instance of time.

- *Exercise.* Estimate the number of atoms N in a 1 cm^3 block of iron, with mass density $\rho = 7.87 \text{ g/cm}^3$ and atomic mass of $m_0 = 55.845 \text{ u}$. (The atomic mass unit is $1 \text{ u} = 1.66 \times 10^{-27} \text{ kg}$.)
- *Answer.* The block has a volume of $V = 1 \text{ cm}^3$. The total mass of the block is $M = \rho V$. One atom weighs on average m_0 , so the total number of atoms is

$$N = \frac{M}{m_0} = \frac{\rho V}{m_0} \quad (2.1)$$

$$= \frac{7.87 \text{ g} \times 1 \text{ cm}^3}{\text{cm}^3 \times 55.845 \times 1.66 \times 10^{-27} \text{ kg}} \quad (2.2)$$

$$= \frac{7.87 \times 10^{-3} \text{ kg} \times 1 \text{ cm}^3}{\text{cm}^3 \times 55.845 \times 1.66 \times 10^{-27} \text{ kg}} \quad (2.3)$$

$$= \frac{7.87 \times 10^{-3}}{55.845 \times 1.66 \times 10^{-27}} \quad (2.4)$$

$$= 8.5 \times 10^{22}. \quad (2.5)$$

Solving that many Newtonian equations, or specifying the initial conditions, or even storing and sensibly interpreting the final outcome, is practically impossible. However, it is also absolutely unnecessary:

Thermodynamic systems consist of a very, very large number of particles N . Experiments performed on macroscopic length and time scales are dominated by the collective behavior of particles, not individual particles. These systems are, therefore, described by a small set of *thermodynamic variables*.

We now discuss the most important thermodynamic variables and how they can be measured.

Volume V . The volume is simply the interior volume of the container that contains the thermodynamic system. If the linear extensions of the system are L_x, L_y, L_z in x, y, z direction, then $V = L_x L_y L_z$. If L_z is changed by an infinitesimal amount dL_z , then this corresponds to a change in volume

$$V \rightarrow V + dV \quad (2.6)$$

with

$$dV = L_x L_y dL_z = L_x L_y L_z \frac{dL_z}{L_z} = V \frac{dL_z}{L_z}. \quad (2.7)$$

Note that on the right hand side it does not matter whether we insert the original volume (V) or the new volume ($V + dV$), because the rules of differential calculus imply

$$dV \, dL_z \approx 0 \quad (2.8)$$

to leading order. The SI unit for volume is m^3 or liter,

$$1 \text{ l} = 1 \text{ dm}^3 = 1 \times (0.1\text{m})^3 = 10^{-3} \text{ m}^3. \quad (2.9)$$

Memorize that 1 liter of water almost exactly weighs 1 kg. 1 quart (= 1 pack of chicken stock) is roughly the same as 1 liter. Another common measure is the gallon,

$$1 \text{ gal} = \begin{cases} 4.5 \text{ l} & (\text{UK, Canada, ...}) \\ 3.8 \text{ l} & (\text{US,...}) \end{cases} = 1 \text{ big milk bottle}. \quad (2.10)$$

To measure the volume of a liquid, one pours it into a container of known linear extensions such as a measuring jug. To measure the volume of a (perhaps weirdly shaped) solid object, one can suspend it into water and then measure the amount of water that has been displaced. Measuring the volume of a gas is more tricky, because gases are *compressible*, i.e. their volume can be changed upon exerting pressure, and their volume stronger depends on temperature. For gas inside a container of known volume V , one always needs to also measure pressure and temperature.

Particle number N . The particle number N remains constant in many elementary thermodynamic processes. (Counter-examples are chemical reactions, or biological systems with osmotic walls which allow particles to leave or enter the system.) Note that N is a dimensionless number, say, $N = 1,999,045,788$. However, chemists like to use a standard unit of particle number, which is the mole.

A *mole* consists of

$$N_A = 6.022 \times 10^{23} \quad (2.11)$$

particles (a dimensionless number!). Compare this to other such conventions: a pair consists of 2 entities, a quartet consists of 4 entities, a dozen consists of 12 entities. In calculations, I recommend to use the dimensionless unit

$$1 \text{ mol} = N_A = 6.022 \times 10^{23} \quad (2.12)$$

to keep track of the number of moles. For instance, the number of iron atoms determined earlier is

$$N = 8.5 \times 10^{22} = 8.5 \times 10^{22} \frac{1 \text{ mol}}{N_A} = 8.5 \times 10^{22} \frac{1 \text{ mol}}{6.022 \times 10^{23}} = 0.14 \text{ mol}. \quad (2.13)$$

The number of moles ν , i.e. the number that satisfies $N = \nu \text{ mol} = \nu N_A$ ($\nu = 0.14$ in the example), is given by

$$\nu = \frac{N}{N_A}. \quad (2.14)$$

The quantity ν is sometimes denoted n in other reference, but not in this lecture! Instead, we will use n to denote the *particle number density*

$$n = \frac{N}{V}. \quad (2.15)$$

For physicists, the introduction of moles is not too useful, and I recommend to always work with N instead of ν . Chemists might find ν more handy for expressing their results. Indeed, the unwieldy atomic mass unit $1 \text{ u} = 1.66 \times 10^{-27} \text{ kg}$ corresponds to a mass per mole given by

$$1 \text{ u} = 1 \text{ u} \frac{N_{\text{A}}}{1 \text{ mol}} = 1.66 \times 10^{-27} \text{ kg} \frac{6.022 \times 10^{23}}{1 \text{ mol}} = 1 \frac{\text{g}}{\text{mol}}, \quad (2.16)$$

which is a decent quantity to work with. The hardly intuitive atomic mass of iron, $m_0 = 55.845 \text{ u}$, becomes

$$m_0 = m_0 \frac{N_{\text{A}}}{1 \text{ mol}} = 55.845 \frac{\text{g}}{\text{mol}}, \quad (2.17)$$

and so on. For a thermodynamic system that consists of one chemical compounds with mass m_0 , the *total mass* of the system is

$$M = Nm_0, \quad (2.18)$$

and the *mass density* is given by

$$\rho = \frac{M}{V} = m_0 n. \quad (2.19)$$

The total mass M of a system can be measured with scales, i.e. by comparing its mass to a reference object whose mass is known. This allows to measure the particle number N if m_0 is known.

Pressure P. The pressure P is defined quite mechanistically as

$$P = \frac{\text{force}}{\text{area}}. \quad (2.20)$$

It can be measured at any spatial position inside the thermodynamic system. When measured at the system boundary, P measures the force exerted by the system onto the container walls. When measured inside the bulk of the system, one should think of a small imagined planar element of area A . The force F exerted by the system onto this plate from one side (which equals the force exerted from the other side), is related to the pressure via $P = F/A$. Constant pressure P means that the amount of force F (in Newton) grows linearly with the area A (in m^2) of the imagined planar element.

A pressure measurement device is called *manometer* or *barometer*. They usually translate the volume measurement of a gas into a pressure. Depending on the context, pressure is measured in many units. The SI unit is Pascal,

$$1 \text{ Pa} = 1 \frac{\text{N}}{\text{m}^2} = \frac{\text{kg}}{\text{m s}^2}. \quad (2.21)$$

Standard atmospheric pressure is

$$1 \text{ atm} = 101.325 \text{ kPa}, \quad (2.22)$$

which is the Earth's average air pressure at sea level. Another popular unit is

$$1 \text{ bar} = 100 \text{ kPa}, \quad (2.23)$$

so that

$$1 \text{ bar} \approx 1 \text{ atm}. \quad (2.24)$$

Other units are Torr or psi (pounds per square inch). Typical car tires have a pressure of

$$34 \text{ psi} = 34 \times 7 \text{ kPa} = 240 \text{ kPa} = 2.4 \text{ atm}, \quad (2.25)$$

whereas bicycles have a wider range, and typically higher pressure.

Temperature T. Temperature is the most interesting variable here. In the kinetic picture, temperature is defined as the *average kinetic energy of a gas of particles*, basically the formula

$$\langle E \rangle = \frac{3}{2} N k_B T, \quad (2.26)$$

which, again, is a mechanistic definition. However, the property "temperature" of a system can be defined purely phenomenologically through the experimentally confirmed zeroth law of thermodynamics. For now, we take for granted that there exist *thermometers*, which are devices which, when brought into contact with a thermodynamic system, display an empirical temperature ϑ . For example, a mercury thermometer displays ϑ through thermal expansion of a mercury column. A gas thermometer measures the temperature T via the variation of volume or pressure of a gas. We call T the absolute temperature. Any two thermometers can be calibrated with each other to determine the function $\vartheta(T)$.

The absolute temperature T is measured in the SI-unit Kelvin. Note that we write (and say)

1 K, <u>not</u> 1°K.	(2.27)
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Temperature differences $\Delta T = T_2 - T_1$ in K are identical when expressed in °C. The freezing and boiling point of water at 1 atm are

$$T_{\text{freeze}} = 0^\circ\text{C} = 273.15 \text{ K}, \quad (2.28)$$

$$T_{\text{boil}} = 100^\circ\text{C} = 373.15 \text{ K}, \quad (2.29)$$

and the absolute zero of temperature corresponds to

$$T = 0 \text{ K} = -273.15^\circ\text{C}. \quad (2.30)$$

Temperatures expressed in degrees Fahrenheit can be converted to degrees Celsius through the rough rule "minus 30, divide by two", for instance

$$70^\circ\text{F} \approx 20^\circ\text{C}, \quad (2.31)$$

$$80^\circ\text{F} \approx 25^\circ\text{C}, \quad (2.32)$$

$$90^\circ\text{F} \approx 30^\circ\text{C}. \quad (2.33)$$

Summary. The main thermodynamic variables are:

- | |
|--|
| <ul style="list-style-type: none"> • volume V • particle number N • particle number density $n = N/V$ • pressure P • temperature T |
|--|

The $6N$ positions and velocities of all particles in a system determine its *dynamical state*. The knowledge of the thermodynamic variables of a macroscopic system are by no means sufficient to determine its dynamical state. For any choice of admissible thermodynamic variables, there is an infinite number of states of atomic or molecular motion that correspond to it. During macroscopic time scales, the system rapidly passes through many of these corresponding dynamical states, while leaving the thermodynamic variables constant.

2.2 States and equilibrium states

The distinction between (general) *thermodynamic states* and (specific) *equilibrium states* of macroscopic systems is a crucial aspect of thermodynamics. This important concept, for instance, needs to be mastered to understand the difference between reversible and irreversible processes later.

A macroscopic system is in a *thermodynamic state* if it can be described by volume, V , and local particle number density, pressure, and temperature, $n(\mathbf{x})$, $P(\mathbf{x})$, $T(\mathbf{x})$, where $\mathbf{x} = (x, y, z)$ is any space point inside the system. More local thermodynamic variables may be needed for more complex system.

What does, say, *local* $T(\mathbf{x})$ mean? We only defined T for large macroscopic systems. While the concept of a local temperature may be intuitive, we need to properly define it. For this note that the number of particles N is usually so large that we can divide the volume V into many smaller compartments of volume $V_0 \ll V$, such that each volume V_0 still contains a macroscopically large number of particles, and hence pressure and temperature are well-defined thermodynamic variables. Furthermore, the compartments can be chosen small enough so that pressure and temperature within each compartment are approximately constant. For any individual compartment at position \mathbf{x}_0 inside the system, we then define

$$n(\mathbf{x}_0) = \frac{N_0}{V_0}, \quad P(\mathbf{x}_0) = P_0, \quad T(\mathbf{x}_0) = T_0, \quad (2.34)$$

where V_0 , N_0 , P_0 , T_0 are the volume, particle number, pressure, and temperature of that individual compartment. By considering all compartments at various locations, we obtain the functions $n(\mathbf{x})$, $P(\mathbf{x})$, $T(\mathbf{x})$.

The thermodynamic variables of a system are usually controlled by *external conditions*. For instance, the volume is determined by the geometry and hence the walls of the container. The temperature can be manipulated through the temperature of the environment. The particle number may be fixed by ensuring that no particles can leave through leaks in the container walls.

An *equilibrium state* of a macroscopic system is a thermodynamic state whose local thermodynamic variables do not vary as long as the external conditions remain unchanged.

The reference to time in this definition, of course, means macroscopic time scales relevant to experiment, not time scales relevant for the microscopic motion of individual atoms or molecules. An equilibrium state can be created in practice by

1. imposing certain external conditions,
2. waiting.

Over a sufficiently long time, the microscopic mechanisms in the system will make it *equilibrate*, i.e. reach the equilibrium state.

In many cases, the external conditions do not impose any spatial variation of the thermodynamic variables inside the system, and the equilibrium states are simply the *homogeneous* states, in which $n(\mathbf{x})$, $P(\mathbf{x})$, $T(\mathbf{x})$ are independent of \mathbf{x} . Non-equilibrium states typically feature *macroscopic currents* as they appear in hydrodynamics.

The following two examples of equilibrium and non-equilibrium states may be instructive.

- *Example 1.* In the *isothermal expansion*, a gas is initially confined to the left one of two equal containers, with a volume V , with constant n, P, T . This is an equilibrium state. The gas is coupled to a heat

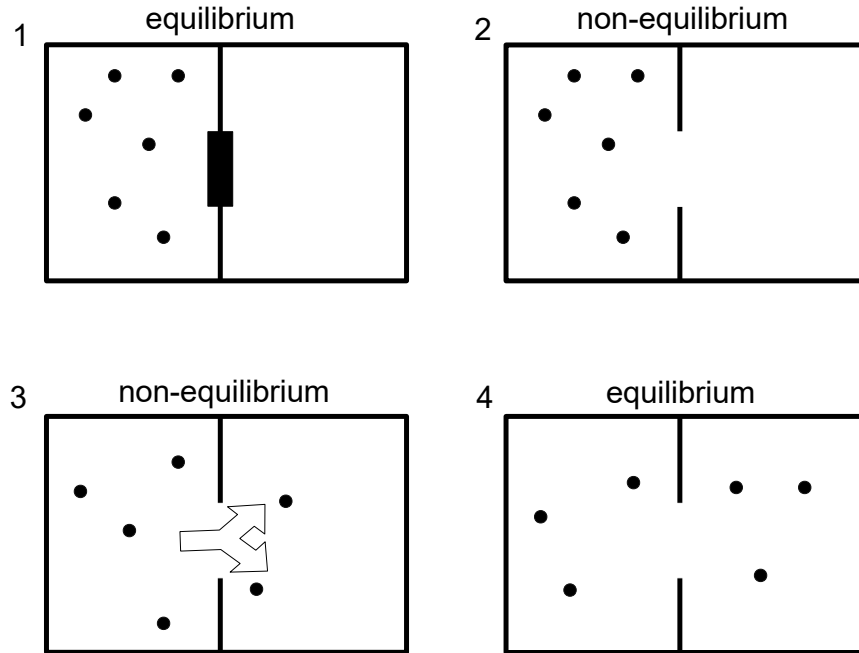


Figure 2.1: Isothermal expansion of a gas (Example 1)

bath that keeps it at a constant temperature.

A wall is removed and the gas can freely expand into the second container, with the total system volume now being $2V$. The temperature does not change in this process because the gas is coupled to the heat bath. After a sufficiently long time the system reaches a new equilibrium state with volume $2V$, density $n/2$, pressure $P/2$, and temperature T .

However, at any intermediate instant of time, the system with volume $2V$ is in a non-equilibrium state with inhomogeneous density and pressure profile, $n(\mathbf{x})$ and $P(\mathbf{x})$. These density and pressure gradients induce macroscopic currents (or flow) in the system.

It is possible to modify the setup so that the intermediate states are also equilibrium states (see below).

- *Example 2.* Consider a homogeneous gas in a volume V with spatially constant n , P , T . If the system is placed in Earth's gravitational field with gravitational force $\mathbf{F} = -m_0 g \hat{\mathbf{z}}$, then the homogeneous state is *not* the equilibrium state. The equilibrium state, instead, has a z -dependent density, pressure, and temperature (barometric height formula).

Note: For most gases, m_0 is much too small to produce a noticeable effect on the length scales of typical laboratory experiments. The gravitational force can then be neglected.

These examples may give the impression that equilibrium states cannot describe thermodynamic systems that "move", meaning that their thermodynamic variables vary in time. This would be bad, since, clearly, a Diesel engine is only useful when it is running. Note, however, that our definition of equilibrium relies on *unchanged external conditions*. In any motor or machine, pistons and the like are moving, so that the external conditions themselves are time-varying.

We can now formulate some important definitions that specify the relation between a thermodynamic system (the "system"), assumed to be contained in a container, and the surrounding of the container (the "environ-

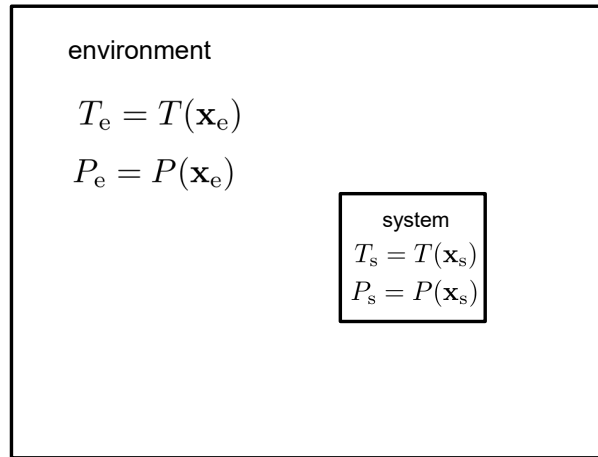


Figure 2.2: System and environment

ment”). Consider the system as a compartment at position \mathbf{x}_s , with system thermodynamic variables

$$T_s = T(\mathbf{x}_s), \quad P_s = P(\mathbf{x}_s), \quad (2.35)$$

and the environment as a compartment at position \mathbf{x}_e , with environment thermodynamic variables

$$T_e = T(\mathbf{x}_e), \quad P_e = P(\mathbf{x}_e). \quad (2.36)$$

We say that the system is *thermally insulated* or *thermally isolated*, if the container walls do not allow heat to be exchanged between the system and the environment. (For instance, a double wall filled with air, which is a bad heat conductor.) In contrast, if the walls allow for heat to be transmitted, such as a thin sheet of metal, we say that system and environment are in *thermal contact* or that they *can exchange heat*.¹ When a system and its environment are in thermal contact, we say that the system is *in thermal equilibrium with its environment* if

$$T_s = T_e. \quad (2.37)$$

When a system and its environment are separated by a *movable wall*, then this wall will be shifted around if the pressures from either side do not match. In this case, we say that they are in *mechanical equilibrium* if

$$P_s = P_e. \quad (2.38)$$

Quite generally, if two systems with temperatures T_1 and T_2 , and pressures P_1 and P_2 , are in equilibrium with each other, then

$$T_1 = T_2, \quad (2.39)$$

$$P_1 = P_2. \quad (2.40)$$

This equilibrium state can only be reached when the two systems are able to “talk to each other” (transfer heat or do work), hence we need thermal contact and movable walls to establish equilibrium.

In the following we will always assume that there is no exchange of particles between the system and the environment. Let us discuss, however, how such an exchange would look like. Assume the system consists of

¹Good heat conductors are heat and stone, bad heat conductors are air, wood, clothes. As a rule of thumb, if something feels cold to the touch, then it is a good heat conductor (heat leaves your hand), whereas if it feels warm, then it is a bad heat conductor (heat stays in your hand).

water, with density $n^{(\text{wat})}$, and the environment contains oil, with density $n^{(\text{oil})}$, both separated by container walls. Then a complete set of thermodynamic variables is $(n^{(\text{wat})}, n^{(\text{oil})}, T, P)$. We assume $T_s = T_e = T$. If the container walls are *impenetrable* for the molecules, then

$$n^{(\text{wat})}(\mathbf{x}_s) = n_s, \quad n^{(\text{wat})}(\mathbf{x}_e) = 0, \quad (2.41)$$

$$n^{(\text{oil})}(\mathbf{x}_s) = 0, \quad n^{(\text{oil})}(\mathbf{x}_e) = n_e. \quad (2.42)$$

On the other hand, if particles can pass through *penetrable or porous walls*, then we eventually reach a state of *chemical equilibrium* with

$$n^{(\text{wat})}(\mathbf{x}_s) = n^{(\text{wat})}(\mathbf{x}_e), \quad (2.43)$$

$$n^{(\text{oil})}(\mathbf{x}_s) = n^{(\text{oil})}(\mathbf{x}_e). \quad (2.44)$$

2.3 Equation of state

So far, we did not say which external condition needs to be changed to specifically modify the pressure. The reason is simple: There is none. The pressure can only be changed indirectly through changing T, N, V .

Consider first a homogeneous system with thermodynamic variables $n = N/V, P, T$. There exists a relation called the *equation of state* which relates these variables according to

$$\phi(n, P, T) = 0. \quad (2.45)$$

Let us give some meaningful examples first:

- *Example 1.* Almost all gases at low pressures and sufficiently far above the condensation temperature are described by the *ideal gas equation of state*

$$PV = Nk_B T \quad (2.46)$$

with Boltzmann's constant $k_B = 1.381 \times 10^{-23}$ J/K. In this example, we have

$$\phi(n, P, T) = P - nk_B T. \quad (2.47)$$

- *Example 2.* When temperature and pressure are such that a real gas is near condensation, deviations from the ideal gas law are observed. A good phenomenological model is then given by the *van-der-Waals equation of state*

$$P = \frac{Nk_B T}{V - bN} - \frac{aN^2}{V^2} \quad (2.48)$$

$$= \frac{nk_B T}{1 - bn} - an^2 \quad (2.49)$$

where a, b are parameters specific to the gas under consideration. In this case,

$$\phi(n, P, T) = (P + an^2)(1 - nb) - nk_B T. \quad (2.50)$$

We will discuss these two examples in more detail later. Some remarks are in order.

- Thermodynamics is a set of general rules and formulas. The equation of state is the *only* point where we specify what substance we are actually dealing with (water, air, iron, ...).
- We always assume that we can solve the equation $\phi(n, P, T) = 0$ to express any of the three variables n, P, T as a function of the remaining two variables. Only two variables of n, P, T are independent.
- The equation of state has been measured for many substances and is stored in databases. Explicit formulas for ϕ exist only in a few cases. Calculation of the equation of state is one of the subjects of statistical mechanics or quantum field theory.
- Often it is assumed that N is constant and the equation of state is then written as

$$\psi(P, V, T) = 0. \quad (2.51)$$

For instance, $\psi(P, V, T) = PV - Nk_B T$ for ideal gases. For fixed N , the thermodynamic state is uniquely determined by any two of the variables P, V, T .

Consider now a macroscopic system in a general thermodynamic state, i.e. it is characterized by the thermodynamic variables $V, n(\mathbf{x}), P(\mathbf{x}), T(\mathbf{x})$. Then at each point \mathbf{x} there is a *local equation of state*

$$\phi(n(\mathbf{x}), P(\mathbf{x}), T(\mathbf{x})) = 0. \quad (2.52)$$

Crucially, the function $\phi(n, P, T)$ is always the same, i.e. it does not depend itself on \mathbf{x} . The \mathbf{x} -dependence is only through its arguments.

For an ideal gas we can write

$$PV = Nk_B T = \frac{N}{N_A} N_A k_B T = \nu RT \quad (2.53)$$

with universal gas constant

$$R = N_A k_B = 8.314 \frac{\text{J}}{\text{K mol}}. \quad (2.54)$$

2.4 Mixtures

Mixtures of several chemical compounds are straightforward to treat within thermodynamics, but due to the increased number of thermodynamic variables, they are a little unwieldy. Here we collect some basic facts.

For a homogeneous macroscopic system that is a mixture of X different chemical compounds, we associate particle numbers $N^{(j)}$ to each of the compounds labelled by an index $j = 1, \dots, X$. The concentration of component j is given by

$$c^{(j)} = \frac{N^{(j)}}{N}, \quad (2.55)$$

with

$$\sum_{j=1}^X N^{(j)} = N, \quad (2.56)$$

$$\sum_{j=1}^X c^{(j)} = 1. \quad (2.57)$$

- *Example.* The chemical composition of air is mostly nitrogen, oxygen, argon, and carbon dioxide, hence $X = 4$ and $j = \text{N, O, Ar, CO}_2$, with concentrations

$$c^{(\text{N})} = 0.7808 = 78.08\%, \quad (2.58)$$

$$c^{(\text{O})} = 0.2095 = 20.95\%, \quad (2.59)$$

$$c^{(\text{Ar})} = 0.0093 = 0.93\%, \quad (2.60)$$

$$c^{(\text{CO}_2)} = 0.0004 = 0.04\%. \quad (2.61)$$

We have

$$\sum_j c^{(j)} = 100\%. \quad (2.62)$$

The relative particle number density of component j is

$$n^{(j)} = \frac{N^{(j)}}{V} = c^{(j)}n, \quad (2.63)$$

with $n = N/V$ the total particle number density. The temperature of the homogeneous system shall be T . Each component j has an equation of state $\phi^{(j)}(n^{(j)}, P^{(j)}, T) = 0$ that is independent of the remaining chemical compounds. If we assume that the interactions between the chemical components j is approximately absent (this need not be the case), then these equations of state remain valid and the *partial pressure* $P^{(j)}$ of the j th compound is found from solving

$$\phi^{(j)}(n^{(j)}, P^{(j)}, T) = 0 \text{ for each } j. \quad (2.64)$$

The total pressure is

$$\sum_{j=1}^X P^{(j)} = P. \quad (2.65)$$

A complete set of thermodynamic variables of the mixture is then

$$(n^{(1)}, \dots, n^{(X)}, P^{(1)}, \dots, P^{(X)}, T). \quad (2.66)$$

Note also that in general each component j has a different mass, $m^{(j)}$, and so $\rho^{(j)} = m^{(j)}n^{(j)}$ for the mass density.

2.5 Extensive and intensive variables

The concept of extensive and intensive variables is very simple, but extremely important and powerful.

Consider a homogeneous thermodynamic system \mathcal{S} described by the thermodynamic variables (V, N, P, T) . Now imagine we would duplicate the system and consider the doubled system as a new thermodynamic system \mathcal{S}' itself. The volume and particle number of this new system will be twice that of \mathcal{S} ,

$$V' = 2V, \quad (2.67)$$

$$N' = 2N. \quad (2.68)$$

The pressure and temperature, however, remain the same regardless of the spatial extent of the system. Hence

$$T' = T, \quad (2.69)$$

$$P' = P. \quad (2.70)$$

Similarly, the particle number density $n = N/V$ remains the same,

$$n' = n. \quad (2.71)$$

A thermodynamic quantity that doubles during an imagined doubling of a homogeneous system is called *extensive*. Examples are V and N . A quantity that remains invariant under an imagined doubling of a homogeneous system is called *intensive*. Examples are P, T, n . The ratio of two extensive quantities is intensive, as is the case for $n = N/V$.

Intensive quantities are usually *local* quantities. Typical examples are *densities*. For instance, the total mass of a system, $M = m_0N$, is an extensive quantity, but the mass density

$$\rho = \frac{M}{V} \quad (2.72)$$

is an intensive quantity. The mass per particle,

$$m_0 = \frac{M}{N}, \quad (2.73)$$

as a ratio of two extensive variables is, of course, also intensive.

If the left-hand-side of an equation is an extensive (intensive) quantity, then the right-hand side must be extensive (intensive) quantity. For instance, for an ideal gas,

$$PV = Nk_B T \text{ (extensive = extensive)} \quad (2.74)$$

$$P = nk_B T \text{ (intensive = intensive)}. \quad (2.75)$$

If you are uncomfortable with doubling a given system \mathcal{S} , you may alternatively divide the system into two macroscopic pieces, $\mathcal{S} = \mathcal{S}_1 \cup \mathcal{S}_2$, by inserting an additional wall. Extensive quantities X then satisfy $X = X_1 + X_2$, whereas intensive quantities Y satisfy $Y = Y_1 = Y_2$.

2.6 Thermodynamic processes and work

Consider a *homogeneous* system in a thermodynamic state with fixed N and equation of state

$$\psi(P, V, T) = 0. \quad (2.76)$$

Choose P, V as the independent variables. It is often convenient to represent them in a *PV-diagram*, with P on the y -axis and V on the x -axis. Any point in the PV-diagram defines a state of the system. The temperature $T = T(P, V)$ is a function of P and V . Points representing states of equal temperature lie on a curve which is called an *isothermal*.

- *Example.* Consider an ideal gas with $PV = Nk_B T$. For fixed N we have

$$T = T(P, V) = \frac{PV}{Nk_B}. \quad (2.77)$$

Isothermal curves in the PV-diagram correspond to

$$P = \frac{Nk_B T}{V} = \frac{\text{const.}}{V}. \quad (2.78)$$

They are hyperbolas having the P - and V -axes as asymptotes.

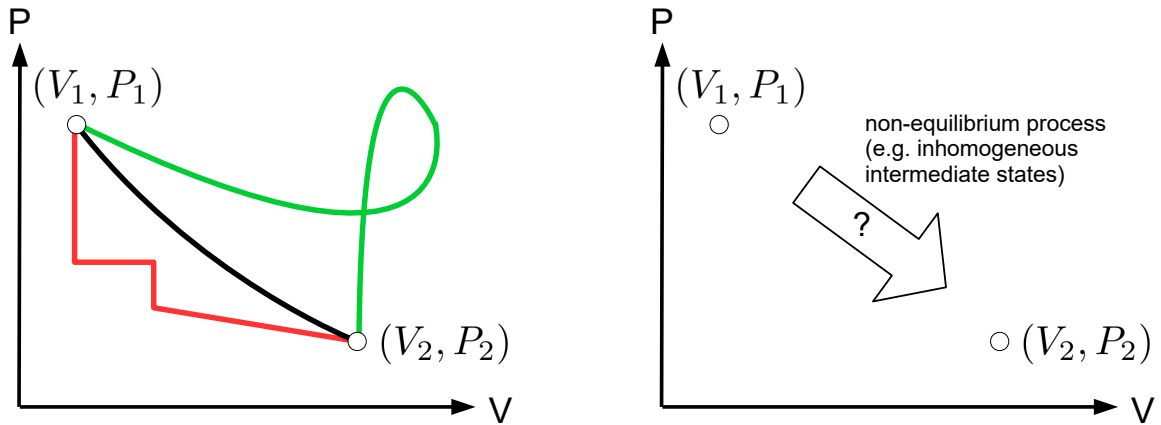


Figure 2.3: *Left.* PV-diagram and three possible transformations connecting the states (V_1, P_1) and (V_2, P_2) . *Right.* A fourth transformation that utilizes non-equilibrium, inhomogeneous intermediate states and thus cannot be drawn in a PV-diagram, because P and V are not defined during the intermediate steps.

We define a *thermodynamic transformation or process* as any transformation that brings a system from an initial state to a final state through a continuous succession of intermediate states. If the initial and final states are represented by two points (V_1, P_1) and (V_2, P_2) in a PV-diagram, then *any* curve connecting these points corresponds to a possible transformation. They correspond to different ways of modifying the external conditions to get from 1 to 2. However, not every transformation connecting 1 to 2 is represented by such a curve.

A transformation is said to be *reversible* when the successive states of the process differ by infinitesimals from *equilibrium states*. In particular, the initial and final states of a reversible transformation need to be states of equilibrium.

If the intermediate states are non-equilibrium states, then they are typically *inhomogeneous*, and so cannot be drawn in a PV-diagram.

We revisit here the central example of reversible vs. irreversible processes. We define a *heat bath* or *heat reservoir* as an environment of temperature T that contains so many particles that its temperature does not change when it is coupled to a (much smaller) system.

Isothermal expansion (irreversible run)

1. Consider a gas inside a container with immovable walls of volume $2V$ coupled to a heat bath of temperature T , so that the system temperature remains constant.
2. Initially, at time $t \leq 0$, a wall separates the left and right halves of the container. An ideal gas of N molecules in the *equilibrium state* (P_i, V, T) occupies the left half. Its pressure is $P_i = Nk_B T/V$.
3. At time $t = 0$, the separating wall is removed.
4. For $t > 0$, volume of the system is $2V$. The system is now in a *non-equilibrium state*, having too high pressure in the left half and almost no pressure in the right half. Rapid macroscopic motions set in to diminish this pressure gradient, creating macroscopic currents of gas. The temperature stays constant due to the coupling to the bath.
5. After a sufficient long time t_{eq} , the gas reaches the final *equilibrium state* $(P_f, 2V, T)$ with pressure $P_f = Nk_B T/(2V) = P_i/2$.

This thermodynamic transformation from (P_i, V) to $(P_f, 2V)$ at constant temperature T is irreversible, since *the intermediate states are far away from equilibrium states*. Practically, it is impossible to start in the final state of the gas occupying both halves of the container and make it move into the left half of the container without any external influence. If you were shown a video recording of the time-interval $t \in [0, t_{\text{eq}}]$, you could tell if the video ran forward or backward. The intermediate states cannot be plotted in a PV-diagram. However, consider now the following modification.

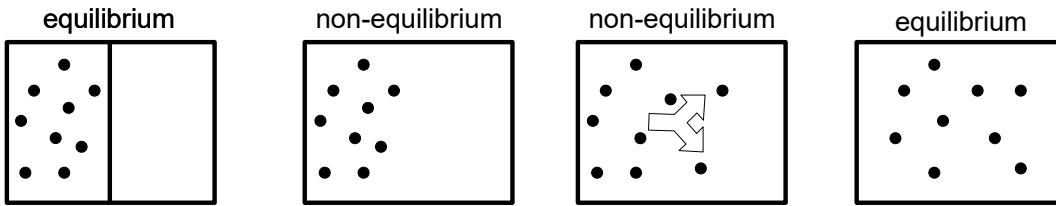
Isothermal expansion (reversible run)

1. As before. However, an externally controlled *piston* is inserted in the right half of the container, initially touching the separating wall.
2. As before.
3. As before.
4. After the separating wall is removed, at $t > 0$, the piston very slowly inches to the right, by an amount $\Delta\ell$ over a time-interval Δt . The speed $\Delta\ell/\Delta t$ is chosen slow enough so that the gas has enough time to adjust itself to the altered external conditions through the usual molecular motion. No macroscopic currents are generated. At each time t , the gas is infinitesimally close to an *equilibrium state*, with a volume $V < V(t) < 2V$, temperature T , and pressure $P_i > P(t) > P_f$.
5. After a certain amount of time t_{tot} , the piston opened up the whole right half of the container, and the gas is in the final equilibrium state $(P_f, 2V, T)$.

This way of performing the isothermal expansion meets all criteria of the definition of a reversible process. And, indeed, it can be reversed: Starting from the final gas occupying the volume $2V$ with pressure P_f , we could slowly move the piston to the left with a negative velocity $-\Delta\ell/\Delta t$, so that the gas is in equilibrium at each time-step. After the amount of time t_{tot} , the gas will be back in the initial state (P_i, V, T) . If you were shown a video recording of the time-interval $t \in [0, t_{\text{tot}}]$, you could *not* tell whether the video ran forward or backward.

The fact that two equilibrium states can be connected by various sorts of processes, some reversible and some irreversible, will be extremely important later on. In a sense, it is at the very heart of thermodynamics. So make sure you understood this example of isothermal expansion.

isothermal expansion (irreversible run)



isothermal expansion (reversible run)

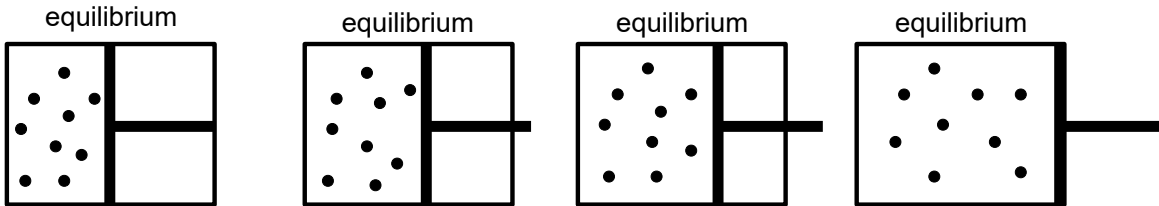


Figure 2.4: Isothermal expansion: irreversible vs. reversible run

During a transformation, the system can perform positive or negative *work*; that is, the system can do work on its surroundings or the surroundings can do work on the system. As an example, we consider a fluid enclosed in a cylinder having a movable piston of area S at one end. If P is the pressure of the fluid against the walls of the cylinder, then $F = PS$ is the force exerted by the fluid on the piston. If the piston is shifted by the gas by an infinitesimal distance dh , then an infinitesimal amount of "work done"

$$dL = F dh = P S dh \quad (2.79)$$

is performed, since the displacement is parallel to the force. But Sdh is equal to the increase in the volume of the system, dV . Thus, we may write

$$dL = PdV. \quad (2.80)$$

For a finite transformation, the work done by the system is obtained by integrating this equation,

$$L = \int_{V_1}^{V_2} P dV. \quad (2.81)$$

Here, 1 and 2 are the initial and final states of the transformation.

Convention. The first law of thermodynamics will be about book-keeping the energy of the system—not of the environment. Therefore, we want to denote every energy unit that increases the system's energy as positive, and every unit that decreases the system's energy as negative. (Think of your bank account.) If a system does work on its environment, it loses energy, so this is a negative contribution. This is logical, but can be cumbersome in some arguments, as we may tend to prefer working with positive quantities.

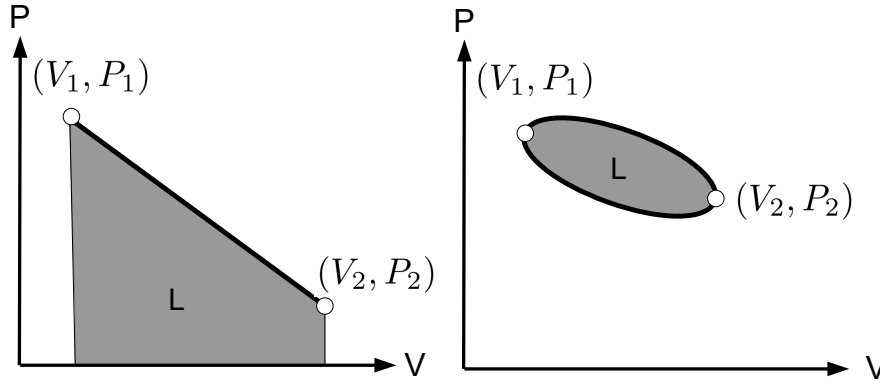


Figure 2.5: Work done $L = -W$ in the PV-diagram. The right figure shows a cyclic transformation.

We will, therefore, use two different symbols: "work" is denoted by the symbol

$$W. \quad (2.82)$$

If the system does work, then $W < 0$, but if work is done on the system so that it gains energy, then $W > 0$. We also say that W is the work performed by external forces. In addition, following Fermi, we define the "work done", meaning the work done by the system, as

$$L = -W. \quad (2.83)$$

If the system does work, then $L > 0$. (L stands for *lavoro*, meaning work in Italian.)

In the reversible example above, the work done was $dL = PdV$, whereas $dW = -PdV$.

For a system whose state can be represented in a PV-diagram during the transformation, the work done during a transformation from state (V_1, P_1) to state (V_2, P_2) has a simple geometric representation: the process is represented by a curve $P(V)$ connecting 1 and 2, the shape of which depends on the type of process considered. The work done during the process is given by the integral

$$L_{1 \rightarrow 2} = \int_{V_1}^{V_2} P(V) dV. \quad (2.84)$$

This integral, and hence the work done, geometrically correspond to the area under the curve in the PV-diagram. If the process can be run in the opposite direction, the work done is the negative of this result,

$$L_{2 \rightarrow 1} = \int_{V_2}^{V_1} P(V) dV = -L_{1 \rightarrow 2}. \quad (2.85)$$

The work performed in a transformation between two states 1 and 2 is typically different for reversible and irreversible runs. For reversible runs we have

$$dL = -dW = PdV \text{ (reversible)}, \quad (2.86)$$

whereas for irreversible runs such a simple formula does not exist.

Consider again the example of isothermal expansion.

Work done in irreversible run. For the irreversible isothermal or "free" expansion, no work is done:

$$L = 0. \quad (2.87)$$

Indeed, after the wall has been removed in 3, while the gas expands into the void, the system volume $2V$ remains constant and there are no movable walls "to be pushed". No work is done.

Work done in reversible run. Now compute the work done in the reversible isothermal expansion from an initial volume V_1 to a final volume $V_2 > V_1$. At each instant of time, the system is homogeneous and can be represented as a state in a PV-diagram. $dL = PdV$ applies at each time. Since T is constant we have

$$P = \frac{Nk_{\text{B}}T}{V}, \quad (2.88)$$

hence

$$L = \int_{V_1}^{V_2} PdV \quad (2.89)$$

$$= Nk_{\text{B}}T \int_{V_1}^{V_2} \frac{1}{V} dV \quad (2.90)$$

$$= Nk_{\text{B}}T \ln V \Big|_{V_1}^{V_2} \quad (2.91)$$

$$= Nk_{\text{B}}T (\ln V_2 - \ln V_1) \quad (2.92)$$

$$= Nk_{\text{B}}T \ln \frac{V_2}{V_1}. \quad (2.93)$$

Since $V_2 > V_1$ we have $L = L_{1 \rightarrow 2} > 0$. The system does work on the piston while expanding. In the reversed run, the piston does work on the system when compressing the gas and $W_{2 \rightarrow 1} > 0$.

Important transformations are those for which the initial and final states are the same. These are called *cyclic processes* or *cycles*. If the state of the system can be represented on a PV-diagram, then a cycle can be represented by a closed curve in this diagram. The work done during one run of the cycle equals the area enclosed by the curve (or the negative thereof, if the cycle is run in the opposite direction).

Recall that processes with $dT = 0$ are called isothermal. Here we extend this list of names according to the following processes:

- $dT = 0$ or $T = \text{const}$: *isothermal*,
- $dP = 0$ or $P = \text{const}$: *isobaric*,
- $dV = 0$ or $V = \text{const}$: *isochore*.

Strictly speaking, isochore refers to $dL = 0$, but usually this means $dV = 0$.

3 First law of thermodynamics

3.1 Conservative and non-conservative forces

We start with a digression into Newtonian mechanics.

Conservative forces. Consider a particle at position $\mathbf{x} = (x, y, z)$ with potential energy $V(\mathbf{x})$. The force acting on the particle at \mathbf{x} is

$$\mathbf{F}(\mathbf{x}) = -\nabla V(\mathbf{x}) = \begin{pmatrix} -\partial_x V(\mathbf{x}) \\ -\partial_y V(\mathbf{x}) \\ -\partial_z V(\mathbf{x}) \end{pmatrix}. \quad (3.1)$$

For example, Earth's gravitational field is $V_{\text{gr}}(\mathbf{x}) = m_0gz$, with m_0 the mass of the particle, and

$$\mathbf{F}_{\text{gr}}(\mathbf{x}) = \begin{pmatrix} 0 \\ 0 \\ -m_0g \end{pmatrix}. \quad (3.2)$$

The electric potential between two electric charges q_1, q_2 is $V_{\text{el}}(\mathbf{x}) = \frac{q_1q_2}{|\mathbf{x}|}$, with $\mathbf{x} = \mathbf{x}_1 - \mathbf{x}_2$ the relative coordinate between the two charges, and

$$\mathbf{F}_{\text{el}}(\mathbf{x}) = \frac{q_1q_2}{|\mathbf{x}|^3} \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \quad (3.3)$$

Forces \mathbf{F}_{gr} and \mathbf{F}_{el} are examples of *conservative forces*, because they can be written as the gradient of some function $-V(\mathbf{x})$. Note that $\mathbf{F} = \mathbf{0}$ is also a conservative force.

Mechanical work. We say that $\mathbf{F}(\mathbf{x})$ is a force field, as it specifies the force on a particle at position \mathbf{x} . In order to move a particle from \mathbf{x} to $\mathbf{x} + d\mathbf{x}$ in a force field $\mathbf{F}(\mathbf{x})$, we need to perform the amount of work

$$dW = \mathbf{F}(\mathbf{x}) \cdot d\mathbf{x}. \quad (3.4)$$

This work could be supplied, for instance, mechanically (say, with our muscles) or electrically. To bring the particle from position \mathbf{x}_A to \mathbf{x}_B , we can divide the path into K sufficiently small steps $\{\Delta\mathbf{x}^{(1)}, \dots, \Delta\mathbf{x}^{(K)}\}$ according to

$$\mathbf{x}^{(1)} = \mathbf{x}_A, \quad (3.5)$$

$$\mathbf{x}^{(2)} = \mathbf{x}_A + \Delta\mathbf{x}^{(1)}, \quad (3.6)$$

$$\vdots \quad (3.7)$$

$$\mathbf{x}^{(k+1)} = \mathbf{x}^{(k)} + \Delta\mathbf{x}^{(k)}, \quad (3.8)$$

$$\vdots \quad (3.9)$$

$$\mathbf{x}^{(K+1)} = \mathbf{x}_B. \quad (3.10)$$

The work required to get from $\mathbf{x}^{(k)}$ to $\mathbf{x}^{(k+1)}$ is

$$\Delta W^{(k)} = \mathbf{F}(\mathbf{x}^{(k)}) \cdot \Delta\mathbf{x}^{(k)}. \quad (3.11)$$

The total work that needs to be performed to get from A to B is

$$W = \sum_{k=1}^K \Delta W^{(k)} = \sum_{k=1}^K \mathbf{F}(\mathbf{x}^{(k)}) \cdot \Delta\mathbf{x}^{(k)}. \quad (3.12)$$

We could make the steps infinitesimal and write

$$W = \int_{\mathbf{x}_A}^{\mathbf{x}_B} dW = \int_{\mathbf{x}_A}^{\mathbf{x}_B} \mathbf{F}(\mathbf{x}) \cdot d\mathbf{x}, \quad (3.13)$$

but the discrete version is absolutely sufficient for now.

- Given two points \mathbf{x}_A and \mathbf{x}_B , there are many possible ways to get from one to the other. Each such way corresponds to a different choice of sufficiently small steps $\{\Delta\mathbf{x}^{(1)}, \dots, \Delta\mathbf{x}^{(K)}\}$, and hence, in principle to a different outcome of the summation that gives W . The value of W , in general, depends on the path we take from \mathbf{x}_A and \mathbf{x}_B .

- The work

$$W = \int_{\mathbf{x}_A}^{\mathbf{x}_B} \mathbf{F}(\mathbf{x}) \cdot d\mathbf{x} \quad (3.14)$$

is independent of the path from \mathbf{x}_A to \mathbf{x}_B if and only if $\mathbf{F}(\mathbf{x})$ is a conservative force.

Non-conservative forces. Typical examples of non-conservative forces are friction, water drag, or air drag. They cannot be written as the gradient of any function. For instance, a friction force acting on a particle may have the form

$$\mathbf{F}(\mathbf{x}, \dot{\mathbf{x}}) = \eta \dot{\mathbf{x}} \quad (3.15)$$

with some friction coefficient η .

Conservation of energy. A mechanical system is called *conservative* if all forces acting on it are conservative forces. The total energy is then the sum of the kinetic and potential energy of all the particles at any given time. It is determined by the dynamical state. The total energy of a conservative system is conserved.

Systems that feature non-conservative forces are called *dissipative*. Energy is still conserved, but only for the total system including its environment. Mechanically, the heat that is created through friction corresponds to disordered motion of particles. This case is captured by the 1st law of thermodynamics.

3.2 Energy and heat

The first law of thermodynamics is essentially the statement of the principle of conservation of energy for thermodynamical systems. It may be expressed by stating that the variation in energy of a system during any transformation is equal to the amount of energy that the system receives from its environment.

Consider first a *conservative* mechanical system of N particles. The system energy is the sum of the potential and the kinetic energy, hence a function of the dynamical state. Assume A and B are two successive states of an isolated system with energies E_A and E_B . If no external forces act on the system, energy remains constant, and

$$E_B = E_A. \quad (3.16)$$

When external forces act on the system, this equality need no longer hold. If W is the work performed by the external forces during a transformation from the initial state A to the final state B , then the conservation of energy implies

$$E_B = E_A + W. \quad (3.17)$$

Importantly, the work done during the transformation only depends on the initial and final states, A and B , not on the particular way in which the transformation from A to B is performed. This is only true for conservative systems.

Conservative systems: The work $W = W_{A \rightarrow B}$ in

$$E_B = E_A + W \tag{3.18}$$

only depends on the initial and final thermodynamic states.

Assume that we find this property contradicted by an experiment performed on a particular thermodynamic system. If we do not wish to discard the principle of conservation of energy, then we must admit the existence of other methods, besides mechanical work, by means of which energy can be exchanged between the system and its environment. Let us consider such an example.

Example. Heating of water

We consider a system composed of a quantity of water of volume V at atmospheric pressure P . We consider two states A and B of the system with temperatures T_A and T_B such that $T_A < T_B$. To a good approximation, these states have the same volume and pressure. [Strictly speaking, B will have a slightly different volume. The volume of water decreases upon heating from 0°C to 4°C (anomaly of water) and then increases when heated beyond 4°C (as in most liquids).]

1. *First way.* We heat the water by placing it over a flame and raise its temperature from the initial value T_A to the final value T_B . The work performed by the system during the transformation is zero, since it does not change its volume, $W = 0$.
2. *Second way.* We raise the temperature of the water from T_A to T_B by heating it by means of friction. For this, we immerse a small set of paddles attached to a central axle into the water, and churn the water by rotating the paddles. We observe that the temperature increases as long as the paddles continue to rotate. This is because the water offers resistance to the motion of the paddles: we must perform positive mechanical work $W > 0$ in order to keep the paddles moving until T_B is reached.

The amount of work W in going from A to B depends on whether we go by means of the first or second way.

Assuming that the principle of conservation of energy holds for our system, then the energy transmitted to the water in the form of mechanical work of rotating paddles in the second way must be transmitted to the water in the first way in a non-mechanical form called *heat*. We are led to the fact that heat and mechanical work are equivalent in this example. They are two different aspects of the same thing, namely, energy.

First law of thermodynamics. We now put all this together into a quantitative formula. We first enclose our system in a cylindrical container with a movable piston at one end. If the container walls are non-heat-conducting, then the system is thermally isolated, and the exchange of energy between the system and the environment can only occur in the form of mechanical work. The amount of work performed on the system, W , when going from state A to state B only depends on the initial and final states of the transformation. Denoting $\Delta E = E_B - E_A$, the work satisfies

$$\Delta E = W. \tag{3.19}$$

(First law of thermodynamics for thermally insulated systems)

If our system is not thermally insulated, this is generally not true, because there can be an exchange of energy

between the system and the environment in the form of heat. We then write the more general equation

$$\Delta E + L = Q, \text{ or} \quad (3.20)$$

$$\Delta E = W + Q, \quad (3.21)$$

(First law of thermodynamics)

where Q is equal to zero for transformations performed on thermally insulated systems and otherwise, in general, is different from zero.

The heat Q can be interpreted physically as the amount of energy that is received by the system in forms other than work.

The first law of thermodynamics is a precise formulation of the equivalence of heat and work.

The work W appearing in the first law could also be electric or magnetic work, but we will mostly be dealing with situations where W is mechanical work.

For a cyclic transformation, the first law takes on a very simple form. Since the initial and final states are the same, we have $\Delta E = 0$, thus

$$L = Q. \quad (3.22)$$

(First law of thermodynamics for cyclic processes)

That is, the work done by a system during a cyclic transformation is equal to the heat absorbed by the system.

The SI unit for energy is Joule,

$$1 \text{ J} = 1 \text{ N m} = 1 \frac{\text{kg m}^2}{\text{s}^2}. \quad (3.23)$$

In the cgs system, the unit of energy is erg, which is obtained from Joule by replacing kg by g, and m by cm, hence

$$1 \text{ erg} = 1 \frac{\text{g cm}^2}{\text{s}^2} = 10^{-7} \text{ J}. \quad (3.24)$$

In the context of power consumption, energy is measured in kWh, with

$$1 \text{ kWh} = 10^3 \frac{\text{J}}{\text{s}} \times 3600 \text{ s} = 3.6 \times 10^6 \text{ J} = 3.6 \text{ MJ}. \quad (3.25)$$

We used the SI unit of power, Watt, $1 \text{ W} = 1 \text{ J/s}$. The average electric energy consumption of a North-American household is $\sim 30 \text{ kWh}$ per day. Another unit, historically defined as the unit of heat, is the *calorie*, 1 cal. Since we know that heat is a form of energy, this means that 1 cal must correspond to a certain amount of Joule. Several definitions of calorie exist, but they all roughly corresponds to the amount of heat needed to heat 1 gram of water at standard atmospheric pressure by 1°C . We have

$$1 \text{ cal} = 4.2 \text{ J}. \quad (3.26)$$

Note that $1 \text{ kcal} = 1000 \text{ cal}$. The "calorie" used to specify the nutritional value of food is actually kcal. Most adults require a diet of about 2000 kcal per day, which amounts to

$$2000 \text{ kcal} = 8.4 \text{ MJ} = 2.3 \text{ kWh}. \quad (3.27)$$

The energy E is an extensive quantity. The energy density E/V and energy per particle E/N are intensive.

3.3 Differentials in thermodynamics

In thermodynamics, we often imagine infinitesimal processes whereupon a quantity, say energy E , changes from a state A to an infinitesimal close (but distinct!) state A' with energy $E' = E + dE$. If we consider a system whose state can be defined by any two of the three variables V, P, T (keeping N constant as usual), then energy, like any other function of the state, is a function of these two chosen variables. This means that, strictly speaking, there are three *functions* called "energy" in the game,

$$E(P, V), E(P, T), E(V, T), \quad (3.28)$$

all representing the same physical observable but through different variables.

Consider a function $f(x, y)$ of two variables x and y . A small change

$$x \rightarrow x' = x + dx, \quad (3.29)$$

$$y \rightarrow y' = y + dy \quad (3.30)$$

implies a change of f according to

$$f' = f(x + dx, y + dy) = f(x, y) + \underbrace{\frac{\partial f}{\partial x}(x, y) \cdot dx + \frac{\partial f}{\partial y}(x, y) \cdot dy}_{df} + \text{higher orders in } dx \text{ or } dy. \quad (3.31)$$

We write this as

$$f' = f + df \quad (3.32)$$

with

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy. \quad (3.33)$$

So far so good.

In thermodynamics, we face the problem that we have three functions $E(P, V)$, $E(P, T)$, $E(V, T)$. So if we quantify the (physically observable!) change $E \rightarrow E' = E + dE$, there are three potential differentials

$$(i) \quad dE = \frac{\partial E}{\partial P} dP + \frac{\partial E}{\partial V} dV, \quad (3.34)$$

$$(ii) \quad dE = \frac{\partial E}{\partial P} dP + \frac{\partial E}{\partial T} dT, \quad (3.35)$$

$$(iii) \quad dE = \frac{\partial E}{\partial V} dV + \frac{\partial E}{\partial T} dT. \quad (3.36)$$

The differentials dE in (i)-(iii) are all *identical*; they describe *the same physical change* in energy $dE = E' - E$, but simply express dE in different variables. There is an ambiguity, however, if we simply write

$$\frac{\partial E}{\partial T}, \quad (3.37)$$

because we do not know if this expression corresponds to the one appearing in (ii) or the one in (iii). We will later see that these two expressions are generally different.

To resolve the ambiguity, we enclose the partial derivative symbol in a parenthesis and place the variable that is to be held constant at the foot of the parenthesis. Thus

$$\left(\frac{\partial E}{\partial T}\right)_V \quad (3.38)$$

means the derivative of E with respect to T while keeping V constant, when T and V are taken as the independent variables. This is in general different from

$$\left(\frac{\partial E}{\partial T}\right)_P, \quad (3.39)$$

in which case the pressure is kept constant. The proper way to write equations (i)-(iii) is then

$$(i) \quad dE = \left(\frac{\partial E}{\partial P}\right)_V dP + \left(\frac{\partial E}{\partial V}\right)_P dV, \quad (3.40)$$

$$(ii) \quad dE = \left(\frac{\partial E}{\partial P}\right)_T dP + \left(\frac{\partial E}{\partial T}\right)_P dT, \quad (3.41)$$

$$(iii) \quad dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT. \quad (3.42)$$

Side comment. Consider a function $F(x)$ and its derivative

$$F'(x) = \frac{dF}{dx}(x). \quad (3.43)$$

A fundamental theorem of calculus states that

$$\int_{x_1}^{x_2} F'(x) dx = F(x_2) - F(x_1). \quad (3.44)$$

We can write this as

$$\int_{x_1}^{x_2} \frac{dF}{dx} dx = F(x_2) - F(x_1), \quad (3.45)$$

or, canceling the factors dx ,

$$\int_{F_1}^{F_2} dF = F_2 - F_1. \quad (3.46)$$

An expression dF that satisfies such an equation is called an *exact differential*, and F is called a *function of state* in the thermodynamic context. Examples of functions of state are V, T, P, E , because they all satisfy

$$\int_{V_1}^{V_2} dV = V_2 - V_1, \quad (3.47)$$

$$\int_{T_1}^{T_2} dT = T_2 - T_1, \quad (3.48)$$

$$\int_{P_1}^{P_2} dP = P_2 - P_1, \quad (3.49)$$

$$\int_{E_1}^{E_2} dE = E_2 - E_1. \quad (3.50)$$

Here, for instance, E_1 and E_2 are the energies in state 1 and 2. In contrast, dW and dQ are *not* exact differentials and W and Q are *not* functions of state. Instead, dW and dQ are merely small quantities and the integrals $\int_1^2 dW$ and $\int_1^2 dQ$ depend on the process or path we choose to connect two thermodynamic states 1 and 2. We have

$$\int_1^2 dW \neq W_2 - W_1, \quad (3.51)$$

$$\int_1^2 dQ \neq Q_2 - Q_1, \quad (3.52)$$

because the object W_1 or “work in state 1” does not exist, etc. Some authors, for this reason, introduce other symbols like δW or δQ to emphasize this difference. We will keep using dW and dQ , always keeping in mind what we just said.

Note also that

$$\int_{E_1}^{E_2} dE = E_2 - E_1 \quad (3.53)$$

implies that for a cyclic process along a closed loop \mathcal{C} in the PV-plane, with $E_2 = E_1$, we have

$$\oint_{\mathcal{C}} dE = 0. \quad (3.54)$$

In contrast,

$$W_{\text{cycl}} = \oint_{\mathcal{C}} dW \quad (3.55)$$

is the total work performed during one cycle. This is generally not zero, otherwise there would be no useful engines.

3.4 Heat capacity and calorimeter

Consider a system described by the variables (V, P, T) . An infinitesimal transformation is a transformation for which the two independent variables change by infinitesimal amounts. The first law of thermodynamics for this transformation reads

$$dE = dW + dQ = -PdV + dQ. \quad (3.56)$$

(First law of thermodynamics for infinitesimal processes)

If we choose T and V as independent variables, E changes according to

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV. \quad (3.57)$$

Inserted into the first law, this yields

$$\left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV = -PdV + dQ, \quad (3.58)$$

or

$$(I) \quad dQ = \left(\frac{\partial E}{\partial T}\right)_V dT + \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] dV. \quad (3.59)$$

Similarly, taking T and P as independent variables we generally have

$$dE = \left(\frac{\partial E}{\partial T}\right)_P dT + \left(\frac{\partial E}{\partial P}\right)_T dP, \quad (3.60)$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad (3.61)$$

which, together with the first law, yields

$$(II) \quad dQ = \left(\frac{\partial E}{\partial T}\right)_P dT + \left(\frac{\partial E}{\partial P}\right)_T dP + PdV \quad (3.62)$$

$$= \left(\frac{\partial E}{\partial T}\right)_P dT + \left(\frac{\partial E}{\partial P}\right)_T dP + P \left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \right] \quad (3.63)$$

$$= \left[\left(\frac{\partial E}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P \right] dT + \left[\left(\frac{\partial E}{\partial P}\right)_T + P \left(\frac{\partial V}{\partial P}\right)_T \right] dP. \quad (3.64)$$

Finally, taking V and P as independent variables we obtain

$$(III) \quad dQ = \left(\frac{\partial E}{\partial P}\right)_V dP + \left[\left(\frac{\partial E}{\partial V}\right)_P + P \right] dV. \quad (3.65)$$

Note, again, that all three expressions for dQ are identical, just expressed in terms of different variables.

Heat capacity. The *heat capacity*, C , of a body is defined as the ratio $C = \frac{dQ}{dT}$, i.e. the infinitesimal amount of heat dQ absorbed by the body as its temperature is increased by the infinitesimal amount dT . In experiments, of course, finite amounts ΔQ and ΔT are used to determine $\Delta Q/\Delta T$. The unit of C is $k_B \propto \text{J/K}$.

In general, the heat capacity of a body will be different according to whether the body is heated at constant volume or constant pressure. We denote this by a subscript according to

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V, \quad (3.66)$$

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P. \quad (3.67)$$

At this point, equations (I) and (II) come in handy. They need to be compared with

$$(I) \quad dQ = \left(\frac{\partial Q}{\partial T}\right)_V dT + \left(\frac{\partial Q}{\partial V}\right)_T dV, \quad (3.68)$$

$$(II) \quad dQ = \left(\frac{\partial Q}{\partial T}\right)_P dT + \left(\frac{\partial Q}{\partial P}\right)_T dP, \quad (3.69)$$

which yields,

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V \stackrel{(I)}{=} \left(\frac{\partial E}{\partial T}\right)_V, \quad (3.70)$$

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P \stackrel{(II)}{=} \left(\frac{\partial E}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P. \quad (3.71)$$

The second term in C_P accounts for the fact that when temperature is increased at constant pressure, the system typically expands and thus performs work. Hence we need to supply additional heat to the system to enable this expansion. In C_V , this term is not present, because the volume is kept constant and so no expansion occurs. Note that the difference between C_P and C_V is largest for gases, whereas liquids and solids expand only moderately when heated.

Specific heat capacity. The heat capacities C_V and C_P are extensive quantities. To get an intensive variable, it is common to divide by the total mass $M = m_0 N$ of the body to obtain the *specific heat capacities*

$$c_V = \frac{C_V}{M}, \quad c_P = \frac{C_P}{M}. \quad (3.72)$$

While the unit of C is J/K, the unit of c is J/(kg K). The ratio

$$\kappa = \frac{C_P}{C_V} = \frac{c_P}{c_V} \quad (3.73)$$

is called heat capacity ratio. c_P and c_V are examples of *material constants*, because they encode information about a specific substance. They are measured and tabulated for most substances. We will meet more material constants later.

Calorimeter. A *calorimeter* is a perfectly thermally isolated container containing two bodies in physical contact with each other, whose individual temperatures are monitored. The device can be used to measure heat in general or the specific heat capacity of one body if it is known for the other body. Typically we have a solid object, initially at temperature T_1 , immersed into a caloric liquid such as water, initially at temperature T_2 . As the two bodies reach thermal equilibrium, they acquire the same temperature T_3 . Let us assume that initially $T_1 > T_2$. Then the water is heated during equilibration from T_2 to T_3 . If we neglect the expansion of water upon heating, then the water absorbs the heat

$$Q = M_{\text{wat}} c_P^{(\text{wat})} (T_3 - T_2), \quad (3.74)$$

where M_{wat} is the total mass of water and $c_P^{(\text{wat})} = 4.182 \text{ J/(gK)}$ is the specific heat capacity of water. To measure the specific heat capacity $c_P^{(\text{sol})}$ of the solid, we neglect the volume contraction of the solid upon cooling, so that $-Q$ is released as heat from the solid into the water. We have

$$-Q = M_{\text{sol}} c_P^{(\text{sol})} (T_3 - T_1), \quad (3.75)$$

hence

$$c_P^{(\text{sol})} = \frac{M_{\text{wat}} (T_3 - T_2)}{M_{\text{sol}} (T_1 - T_3)} c_P^{(\text{wat})}. \quad (3.76)$$

3.5 Application of the first law to gases

Recall that we earlier said that the expression

$$\frac{\partial E}{\partial T} \quad (3.77)$$

makes no sense, as we need to indicate whether V or P is held fixed. However, for an ideal gas, both expressions actually agree,

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V \stackrel{\text{ideal gas}}{=} \left(\frac{\partial E}{\partial T} \right)_P. \quad (3.78)$$

When expressed in terms of the variables (V, T) or (P, T) , the energy of an ideal gas is a function of T alone,

$$E(V, T) = E(P, T) = E(T). \quad (3.79)$$

As usual, we consider N as a constant. Another way to write this is

$$dE = C_V dT. \quad (3.80)$$

This property of ideal gases can be derived from statistical mechanics, and is approximately still valid for real gases. Here we derive this result from an experimental observation.

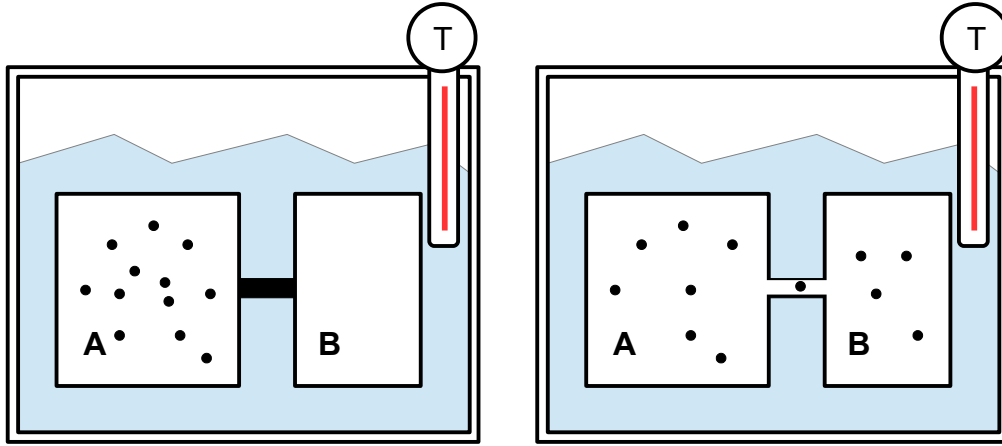


Figure 3.1: Expansion of an ideal gas does not change the temperature of the water in the calorimeter.

Experiment. Expansion of an ideal gas

We consider a calorimeter, i.e. a perfectly thermally isolated container filled with water. Into it we place another container having two chambers, A and B , connected by a tube. Chamber A is filled with a gas and chamber B is evacuated, the two chambers are initially shut off from each other by a closed valve in the connecting tube.

1. First we wait sufficiently long until thermal equilibrium between the chambers and the water has set in. For this we monitor the temperature of the water with a thermometer. If the temperature remains constant over an extended period of time, we are in equilibrium.
2. We then open the valve to connect the two chambers, thus permitting the gas to flow from A into B until the pressure everywhere in the chambers is the same.
3. We observe only a slight change in the reading of the thermometer.

The observation made in 3 implies that there had been practically no transfer of heat from the caloric water to the chambers or vice versa. It is assumed that if this experiment could be performed with an ideal gas, there would be no change at all.

We now apply the first law to the transformation. Since we observe $Q = 0$ between the gas and the water, the gas enclosed in the chambers behaves like a thermally isolated system and we have

$$\Delta E + L = 0. \tag{3.81}$$

Since the total volume of the chambers does not change (no movable walls), the gas cannot perform any work, and so $L = 0$. Therefore,

$$\Delta E = 0. \tag{3.82}$$

The energy of the gas does not change.

During the transformation, however, the volume of the gas changed from A to $A + B$. Since there was no variation in energy during the process, we conclude that a variation in volume at constant temperature produces no variation in energy,

$$\left(\frac{\partial E}{\partial V}\right)_T = 0. \tag{3.83}$$

In other words, the energy of an ideal gas is a function of the temperature only and not a function of the volume. Similarly, the experiment showed that the change in pressure during the isothermal expansion had no effect on the energy, so

$$\left(\frac{\partial E}{\partial P}\right)_T = 0. \quad (3.84)$$

This completes our proof.

Implication 1. We first determine the form of the function $E(T)$. We make use of the additional experimental fact that C_V of a gas only slightly depends on temperature. Integrating the equation

$$dE = C_V dT \quad (3.85)$$

we obtain

$$E(T) = C_V T. \quad (3.86)$$

We have set the integration constant E_0 , which would be the energy at $T = 0$, to zero.

Implication 2. We next compute C_P for the ideal gas. Recall that

$$C_P = \left(\frac{\partial E}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P. \quad (3.87)$$

The first term is identical to C_V for an ideal gas. For the second term we use $PV = Nk_B T$ to arrive at

$$C_P = \left(\frac{\partial E}{\partial T}\right)_V + P \frac{\partial}{\partial T} \left(\frac{Nk_B T}{P}\right) \quad (3.88)$$

$$= C_V + Nk_B. \quad (3.89)$$

Using kinetic theory one can show that

$$C_V = \frac{3}{2} Nk_B \text{ for a monoatomic gas,} \quad (3.90)$$

$$C_V = \frac{5}{2} Nk_B \text{ for a diatomic gas.} \quad (3.91)$$

For an ideal gas we then have

$$E(T) = \frac{3}{2} Nk_B T \text{ for a monoatomic gas,} \quad (3.92)$$

$$E(T) = \frac{5}{2} Nk_B T \text{ for a diatomic gas.} \quad (3.93)$$

Expressed in terms of (P, V) this becomes

$$E(P, V) = \frac{3}{2} PV \text{ for a monoatomic gas,} \quad (3.94)$$

$$E(P, V) = \frac{5}{2} PV \text{ for a diatomic gas.} \quad (3.95)$$

We further have

$$C_P = \frac{5}{2} Nk_B \text{ for a monoatomic gas,} \quad (3.96)$$

$$C_P = \frac{7}{2} Nk_B \text{ for a diatomic gas,} \quad (3.97)$$

and

$$\kappa = \frac{5}{3} \text{ for a monoatomic gas,} \quad (3.98)$$

$$\kappa = \frac{7}{5} \text{ for a diatomic gas.} \quad (3.99)$$

3.6 Adiabatic transformations of a gas

A transformation is called *adiabatic* if the following two conditions are satisfied:

1. The transformation is reversible.
2. The system is thermally insulated so that no heat can be exchanged between the system and the environment.

Condition 2 implies that $dQ = 0$ during the transformation and that the first law reads $\Delta E + L = 0$ for adiabatic processes.

We can expand or compress a gas adiabatically by enclosing it in a cylinder with non-heat-conducting walls (condition 2) and a movable piston on one end, and very slowly shifting the piston inward and outward. In this case, the gas molecules have enough time to adjust to the small gradual volume changes during the process, and we effectively are in an equilibrium state at any time, hence the transformation is reversible (condition 1).

Now would be a good point to recall the reversible run of the isothermal expansion.

A gas that expands adiabatically does external work, so L is positive in the first law. Hence, ΔE must be negative, and the energy of a gas decreases during an adiabatic expansion. Since the energy is related to the temperature through $E = C_V T$ for an ideal gas (or a similar relation for real gases), a decrease in energy means a decrease in temperature of the gas.

Using $dE = C_V dT$ for ideal gases we have

$$C_V dT + P dV = 0. \quad (3.100)$$

Using the equation of state $PV = Nk_B T$, we can eliminate the pressure to obtain

$$C_V dT + \frac{Nk_B T}{V} dV = 0, \quad (3.101)$$

or

$$\frac{dT}{T} + \frac{Nk_B}{C_V} \frac{dV}{V} = 0. \quad (3.102)$$

Integration yields

$$\ln T + \frac{Nk_B}{C_V} \ln V = \text{const.} \quad (3.103)$$

We can write this as

$$TV^{\frac{Nk_B}{C_V}} = \text{const}, \quad (3.104)$$

or, using $C_P = C_V + Nk_B$ and $\kappa = C_P/C_V$, as

$$TV^{\kappa-1} = \text{const.} \quad (3.105)$$

(Adiabatic transformation of an ideal gas)

Using $PV = Nk_{\text{B}}T$ we readily find that

$$PV^{\kappa} = \text{const.}, \quad (3.106)$$

$$T^{\kappa} P^{1-\kappa} = \text{const.} \quad (3.107)$$

Note that in a PV-diagram, an isothermal transformation is given by $PV = \text{const.}$ Hence, a curve corresponding to an adiabatic transformation is *steeper than an isotherm in the PV-diagram* due to $\kappa > 1$.

4 Second law of thermodynamics

4.1 Perpetuum mobile

A *perpetuum mobile* (Latin for "perpetual mover") or *perpetual motion machine* is an impossible machine that operates in cycles and, once started, would run forever and do work.

The first law of thermodynamics rules out the possibility of constructing a perpetuum mobile.

For one, in a thermally isolated system, the energy does not change in a cycle, and due to the 1st law the work done is zero. When including the environment into the setting, any machine supplied with a finite amount of energy at a given time will eventually stop because over time energy is lost to heat due to friction. The 1st law forbids a machine that creates energy, which it could use to compensate this friction loss or do work.

The first law does not limit the possibility of transforming one form of energy into the other, such as transforming work into heat and heat into work, as long as the total amount of energy remains constant. Indeed, we can always transform work into heat, for instance, by using friction to turn mechanical work into an equal amount of heat, or using electric currents to heat up a resistance element, thus transforming electrical work into heat.

Work can, in principle, to 100% be converted into heat.

However, one experimentally observes definite limitations to the possibilities of transforming heat into work. If this were not the case, we could construct a machine that continuously absorbs heat from its environment and uses this heat to perform work. Since the amount of thermal energy in the soil, water, atmosphere is practically unlimited, such a machine would effectively be operating like a perpetuum mobile. Therefore, it is called a *perpetuum mobile of the second kind*.

The second law of thermodynamics rules out the possibility of constructing a perpetuum mobile of the second kind. It implies limits on what fraction of heat can (at best) be converted into work.

Some examples of perpetuum mobiles of the second kind: Drive a ship across the ocean only by converting heat extracted from the water into work of the propellers. Light a light bulb or heat a pot by extracting heat from the surrounding air.

4.2 Carnot cycle

We defined a *heat bath* or *heat reservoir* as a large body of temperature T that contains so many particles that its temperature does not change when it is coupled to a system. It is used to *bring and keep* the system to the temperature T through thermal contact and heat transfer.

In principle, the heat bath could exchange both heat Q and work W with the system. If the heat bath is such that it cannot perform work on the system, it is called a *heat source*.

A system may be coupled to several reservoirs, or to different reservoirs at different times. The *Carnot cycle* uses two heat sources, with temperatures T_1 (lower) and T_2 (higher). To memorize the lower and higher temperatures in the following, use that $2 > 1$. It is a reversible cycle built from two isothermal lines and two adiabatic lines, intersecting at four points A, B, C, D . We use variables (V, T) to label these states.

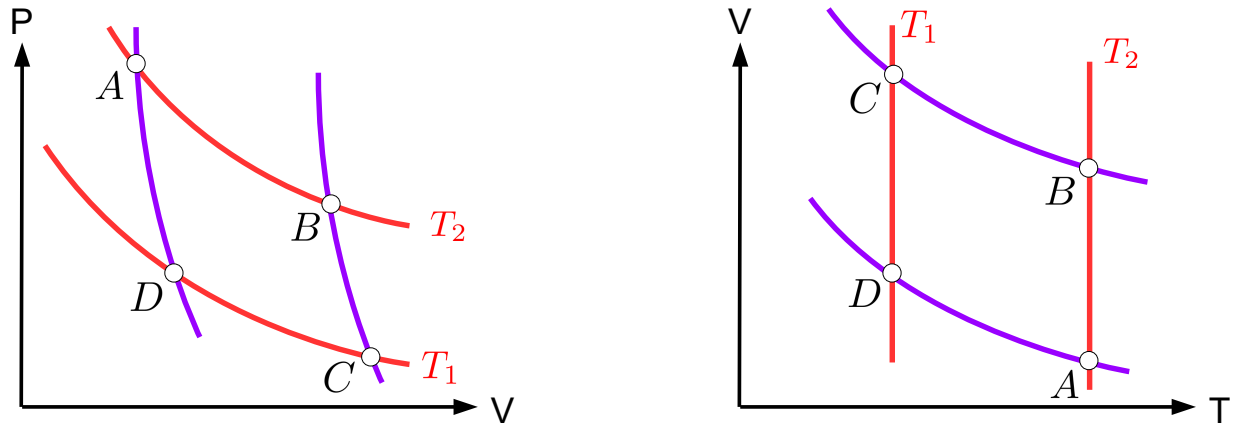


Figure 4.1: Carnot cycle, schematic, in the PV-diagram (left) and VT-diagram (right)

Carnot cycle

Consider a system whose initial state is A , with volume V_A at temperature T_2 . The Carnot cycle is the following set of transformations that are supposed to be performed *reversibly*.

$A \rightarrow B$. Isothermal expansion to volume V_B at fixed temperature T_2 .

$B \rightarrow C$. Adiabatic expansion to volume V_C . During that, temperature decreases to T_1 .

$C \rightarrow D$. Isothermal compression to volume V_D at fixed temperature T_1 .

$D \rightarrow A$. Adiabatic compression to volume V_A . During that, temperature increases to T_2 .

Important for the Carnot cycle is that these transformations are performed reversibly, i.e. slow enough so that the system is infinitesimally close to an equilibrium state at each intermediate step.

Example of a Carnot cycle. Consider a fluid enclosed in a cylindrical container with isolating side wall and a movable isolating piston on the top. Heat can only be transferred through the base of the cylinder, which we take to be heat-conducting. There are two heat sources, with temperatures T_1 and T_2 , such that $T_2 > T_1$.

1. Initially the fluid is assumed to have volume V_A and temperature T_2 (corresponding to some pressure P_A via the equation of state).
2. Place the system on the heat source T_2 . No heat transfer will occur initially.
3. Keeping the system on the heat source, we slowly (reversibly) raise the piston until the volume reaches V_B . The heat source ensures that the fluid remains at temperature T_2 .
4. Remove the system from heat source T_2 and place it on an insulator. We continue to slowly raise the piston until we reach volume V_C . The fluid is thermally insulated and cannot absorb heat, hence cools to temperature T_1 during that process.
5. Now place the system on heat source T_1 . No heat transfer will occur initially.
6. Slowly press down the piston until we reach volume V_D . The heat source ensures that the temperature of the fluid remains T_1 .
7. Remove the system from heat source T_1 and place it on an insulator. Continue to slowly compress until volume V_A is reached. Since the fluid is thermally insulated and cannot release heat, it heats up to temperature T_2 during the process.

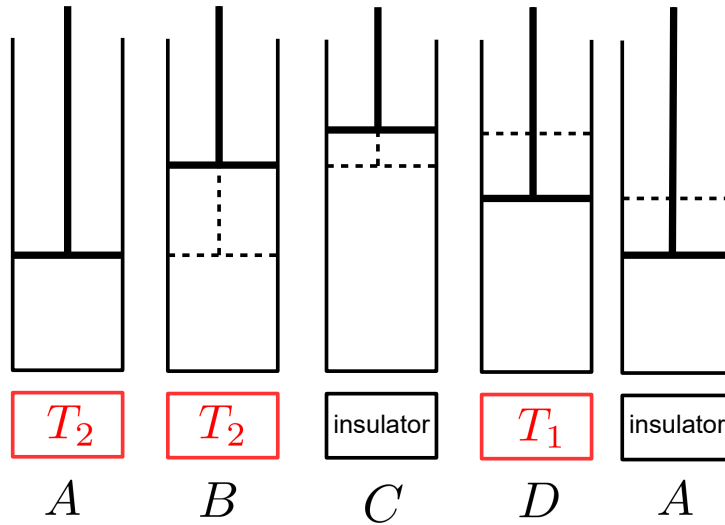


Figure 4.2: Example of a Carnot cycle discussed in the text

Heat and work. During the isothermal expansion $A \rightarrow B$, the system absorbs an amount of heat $Q_2 > 0$ from the source T_2 . Similarly, during the isothermal compression $C \rightarrow D$, it releases an amount of heat $Q_1 > 0$ to the source T_1 (it absorbs an amount $-Q_1$ from source T_1). No heat is transferred in the adiabatic sections. Hence the total amount of heat absorbed by the system during the cycle is $Q_2 - Q_1$. The amount of work done L during one cycle, given by the area enclosed in the PV-diagram, follows from the 1st law for cycles to be

$$L = Q_2 - Q_1. \quad (4.1)$$

This equation means that only a fraction of the heat absorbed from the hot source at T_2 is transferred into work L in the Carnot cycle. The part Q_1 , instead of being transformed into work, is surrendered to the source at temperature T_1 . We define the *efficiency* of the Carnot cycle as the ratio

$$\eta = \frac{L}{Q_2}. \quad (4.2)$$

It represents the fraction of heat that is converted into work. We have

$$\eta = 1 - \frac{Q_1}{Q_2} \quad (4.3)$$

for the Carnot cycle, so the portion $\propto Q_1$ is not transformed into work.

Since the Carnot cycle is reversible, it can be run in the opposite direction, $A \rightarrow D \rightarrow C \rightarrow B \rightarrow A$. It then absorbs the work L , and absorbs the amount of heat Q_1 from source the colder T_1 , whereas it gives up the amount of heat Q_2 to the hotter source T_2 .

4.3 Statement of the second law

We state the 2nd law in two forms and prove their equivalence.

Second law of thermodynamics (Kelvin's formulation)

There is no transformation whose only final result is to completely transform heat extracted from a heat source at constant temperature into work.

The word "only" is important here. For one, (i) it *is* possible to completely transform heat from a source at constant temperature into work, provided some other change in the state of the system is present at the end of the process. Furthermore, (ii) if some heat is released to another body during the process, then the conversion of heat to work is not the only final result.

Example for (i). In the reversible run of the isothermal expansion of an ideal gas, an amount of heat Q is supplied by the heat source to keep the gas at T . Since $E(V, T) = E(T)$ for a gas, its energy does not change, $\Delta E = 0$. Consequently $L = Q$. The heat is completely transformed into work. However, this is not the only final result of the process, because at the end of the process the gas occupies a larger volume than at the beginning.

The fact that the initial and final state differ in this (or any similar) example, makes it impossible to use such a transformation to form a *cycle* that is run several times, which would then constitute a perpetual mobile of the second kind.

Example for (ii). The Carnot process is a cycle, so initial and final states are the same, which extracts heat Q_2 from a source and performs work L . However, it only converts a fraction of the heat into work, $L = Q_2 - Q_1$, while it dumps the amount of heat Q_1 into another body. Hence the conversion of heat into work is not the only final result, but there is another final result, namely the rejection of some heat Q_1 . The coefficient η between extracted heat and performed work in $L = \eta Q_2$ is precisely the efficiency. Hence Kelvin's statement implies $\eta < 1$ for all cyclic processes.

The word "completely" is, strictly speaking, superfluous and implied by "only", see example (ii). If the conversion of heat into work is not complete, then there must always be some rejected heat as an additional final result of the process.

The wording is to suggest that a positive amount of heat $Q > 0$ is absorbed by the system and converted into a positive work done $L > 0$. If $L < 0$, i.e. work $W > 0$ is performed on the system, then the system could convert this work via friction into negative heat $Q = -W < 0$ that is released into the environment. We then have a situation where the only final result is that work is completely converted into heat. No constraint arises in this case, because work can always be completely converted into heat.

Second law of thermodynamics (Clausius's formulation)

There is no transformation whose only result is to transfer heat from a body at a given temperature to a body at a higher temperature.

Clausius's statement implies that some work must be performed in order to transfer heat from a colder body to a hotter body. This work requires an external energy source, so that the supply of energy through work is an additional final result of the process. Refrigerators, of course, operate in this way and are not forbidden by the 2nd law of thermodynamics.

We prove the equivalence of Kelvin's and Clausius's statements. We use contraposition, i.e. to prove $X \Rightarrow Y$, we show $\text{not-}Y \Rightarrow \text{not-}X$.

not-Kelvin \Rightarrow not-Clausius. Assume Kelvin's statement is wrong. We can then perform a transformation which extracts an amount of heat from a source "1" at temperature T_1 , and whose only final result is to completely transform this amount of heat into work. By means of friction, we could completely transform this work into heat again, and use this heat to heat up another body "2" that is at any temperature T_2 . In particular, this would also work if $T_2 > T_1$. The only final result of this whole process would then be to

transfer heat from a body "1" at temperature T_1 to a body "2" at higher temperature T_2 . Hence Clausius's statement is wrong.

not-Clausius \Rightarrow *not-Kelvin*. Assume Clausius's statement is wrong. We can then transfer an amount of heat Q_2 from a heat source "1" at temperature T_1 to a body "2" at higher temperature T_2 . We next use a Carnot process to absorb the same heat Q_2 from source "2" at the high temperature (during step $A \rightarrow B$) and transform it into work L . During the Carnot process, some amount of heat Q_1 is dumped into "1" at the lower temperature. Since body "2" absorbed and released the same amount of heat, there is no overall change to body "2" in the process. The net amount of heat extracted from "1" is $\Delta Q = Q_2 - Q_1$, which is completely transformed into work $L = \Delta Q$. Hence we constructed a process which extracts an amount of heat ΔQ from the source "1" at constant temperature and transformed it completely into work. Thus Kelvin's statement is wrong.

Note that we have only shown the equivalence of both formulations of the 2nd law, we did not "prove" it. Its experimental justification comes from the fact that no-one ever accomplished to construct a perpetual mobile of the second kind, or observed heat to flow from a cold to a hot body by itself.

4.4 Heat engines and refrigerators

A machine that uses the flow of heat from a body at higher temperature T_2 to a body at lower temperature T_1 to perform work is called a *heat engine*. Denote the amount of heat per cycle extracted from body "2" by Q_2 and the amount of heat per cycle submitted to body "1" by Q_1 . The work performed per cycle is $L = Q_2 - Q_1 > 0$. We define the *efficiency of a heat engine* by

$$\eta = \frac{L}{Q_2} = 1 - \frac{Q_1}{Q_2}. \quad (4.4)$$

Crucially, the underlying cycle *need not be reversible or a Carnot cycle*. An engine using a reversible cycle will be called reversible engine.

Note that $\eta = L/Q_2$ is the fraction of heat converted into work. The closer η is to 100%, the better for applications. Kelvin's statement implies $\eta < 1$. In the following two sections, we show that the efficiency of *any* reversible engine operating between T_2 and T_1 is identical, and satisfies

$$\eta_{\text{rev}} = 1 - \frac{T_1}{T_2}. \quad (4.5)$$

Typically the body at lower temperature, into which the amount of heat $Q_1 > 0$ is dumped and lost, is the environment of the engine, thus we usually cannot control T_1 . In practice, it would be difficult to run an engine with very low $T_1 \rightarrow 0$, since we continuously dump heat into "1". To get a large efficiency, we want T_2 to be as high as possible. Of course, any actual efficiency will generally be lower than η_{rev} , because all actual heat engines are far from being reversible. In fact, we will show that

$$\eta \leq \eta_{\text{rev}} \quad (4.6)$$

in general.

We first show that if $L > 0$, then we have $Q_2 > 0$ and $Q_1 > 0$. Assume first that $Q_1 \leq 0$. This means the engine absorbs the positive amount of heat $|Q_1| = -Q_1$ from heat source "1". We could then use the hotter source "2" to heat up source "1" to exactly compensate for the lost amount of heat $|Q_1|$. Indeed, this would amount to heat flowing from a hot to a cold body, which is not forbidden by the 2nd law. During one cycle, there would then be no change to source "1". Furthermore, the amount of heat effectively absorbed from source "2" by the engine is $Q_2 + |Q_1|$, which is fully converted into work $L = Q_2 - Q_1 = Q_2 + |Q_1|$. Since

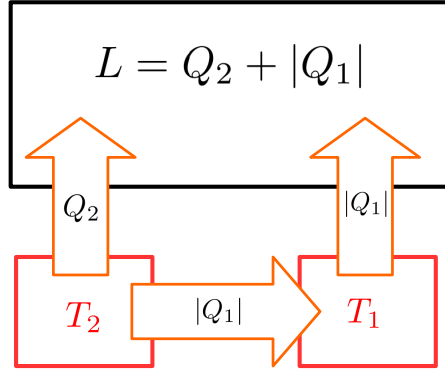


Figure 4.3: Assuming $Q_1 \leq 0$ in heat engines leads to a contradiction.

this is the only result of the cycle, this is in contradiction to Kelvin's formulation of the 2nd law. Hence $Q_1 > 0$. Since $L > 0$, we immediately get $Q_2 > 0$. \square

In the following, we consider two engines that operate between the same temperatures T_1 and T_2 . The first engine shall be characterized by (L, Q_1, Q_2) , the second engine by (L', Q'_1, Q'_2) . We show the following fundamental theorem:

A. If the first engine is reversible, then

$$\frac{Q_2}{Q_1} \geq \frac{Q'_2}{Q'_1}. \quad (4.7)$$

B. If both engines are reversible, then

$$\frac{Q_2}{Q_1} = \frac{Q'_2}{Q'_1}. \quad (4.8)$$

Note that B implies that η_{rev} is identical for all reversible engines operating between T_1 and T_2 , whereas A implies $\eta \leq \eta_{\text{rev}}$. The second engine in A need not be reversible.

Statement A implies B, because if A is true and if the second engine is also reversible, then we obtain the relation with both " \leq " and " \geq ", hence $\frac{Q_2}{Q_1} = \frac{Q'_2}{Q'_1}$ in this case.

It remains to show A. For both engines we have

$$L = Q_2 - Q_1, \quad (4.9)$$

$$L' = Q'_2 - Q'_1. \quad (4.10)$$

The ratio Q_2/Q'_2 can to arbitrary precision be approximated by a rational number

$$\frac{Q_2}{Q'_2} = \frac{N'}{N}, \quad (*) \quad (4.11)$$

where N, N' are positive integers. Now consider a *combined cycle* that consists of N' runs of the second engine and N runs of the reversed first engine. (This is permissible, since the first engine is reversible.) When operated in the reverse, the first engine absorbs an amount of work L , gives up the amount of heat

Q_2 to source "2", and receives the amount of heat Q_1 from source "1". The total amount of work done by the combined engine is

$$L_{\text{total}} = N'L' - NL, \quad (4.12)$$

the total amount of heat received from source "2" is

$$Q_{2,\text{total}} = N'Q'_2 - NQ_2, \quad (4.13)$$

and the total amount of heat given to source "1" is

$$Q_{1,\text{total}} = N'Q'_1 - NQ_1. \quad (4.14)$$

This yields

$$L_{\text{total}} = Q_{2,\text{total}} - Q_{1,\text{total}}. \quad (4.15)$$

However, equation (*) implies $Q_{2,\text{total}} = 0$ and so

$$L_{\text{total}} = -Q_{1,\text{total}}. \quad (4.16)$$

Importantly, at this point we do not know the sign of L_{total} (which is the sign of $-Q_{1,\text{total}}$). The combined cycle is constructed such that there is no change to source "2" after the whole cycle. If $L_{\text{total}} > 0$, then the only final result of the combined cycle is that the heat absorbed from source "1" at constant temperature T_1 (which is $-Q_{1,\text{total}}$) is converted into the work L_{total} . This contradicts Kelvin's statement. However, if $L_{\text{total}} \leq 0$, then work is performed on the engine, and the engine converts this work completely into the amount of heat $|Q_{1,\text{total}}|$ that is dumped into source "1". Nothing limits the conversion of work into heat. Hence

$$L_{\text{total}} \leq 0 \quad (4.17)$$

and

$$0 \leq Q_{1,\text{total}} = N'Q'_1 - NQ_1 = N\left(\frac{Q_2}{Q'_2}Q'_1 - Q_1\right). \quad (4.18)$$

Hence

$$\frac{Q_2}{Q_1} \geq \frac{Q'_2}{Q'_1}, \quad (4.19)$$

which proves A. \square

A *refrigerator* is a heat engine run in the reverse direction, which extracts an amount of heat Q_1 from a source at low temperature T_1 by absorbing work $W > 0$, and dumps an amount of heat Q_2 to a source at higher temperature T_2 . (If the emphasis is on heating the hotter source, it is equivalently called a *heat pump*.) The work $W > 0$ is required by Clausius' formulation of the 2nd law. The *coefficient of performance* is given by

$$\text{COP} = \frac{Q_1}{W} > 1. \quad (4.20)$$

For a reversible refrigerator (such as a reverse Carnot cycle) we have

$$\text{COP}_{\text{rev}} = \frac{T_1}{T_2 - T_1} \quad (4.21)$$

For instance, for $T_2 = 20^\circ\text{C}$ we have

$$T_1 = 3^\circ\text{C} \Rightarrow \text{COP}_{\text{rev}} = 16, \quad (4.22)$$

$$T_1 = -18^\circ\text{C} \text{ (freezer)} \Rightarrow \text{COP}_{\text{rev}} = 6.7, \quad (4.23)$$

whereas real household refrigerators have $\text{COP} \sim 2$.

4.5 Zeroth law of thermodynamics

To formally define the concept of *temperature*, without resorting to kinetic theory or statistical mechanics, one may use the zeroth law of thermodynamics. It is the following postulate that is confirmed by experiment:

When two thermodynamic systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.

Note the word "thermal" here. This postulate implies that there is a property of thermodynamic systems which is common to all systems in thermal equilibrium. This quantity serves as an empirical temperature \tilde{T} .

Let us call the systems A, B, C . For concreteness we may think of C as a thermometer. The volume and pressure of each system are (V_A, P_A) , (V_B, P_B) and (V_C, P_C) .

1. We assume that A and C are in thermal contact through a heat-conducting wall. For general values of (V_A, P_A, V_B, P_B) , they would not be in thermal equilibrium. Instead, in thermal equilibrium there will be a constraint of the form

$$f_1(V_A, P_A, V_C, P_C) = 0 \quad (4.24)$$

relating the four quantities through some function f_1 . We want to show that this relation is actually of the form

$$\tilde{T}_A(V_A, P_A) = \tilde{T} = \tilde{T}_C(V_C, P_C). \quad (4.25)$$

We could then define \tilde{T} as temperature read off from the thermometer C . Furthermore, the relation $\tilde{T} = \tilde{T}_A(V, P)$ constitutes the equation of state for system A , similarly for C .

2. To show Eq. (4.25), we also consider B and C , whose thermal equilibrium implies a relation of the form

$$f_2(V_B, P_B, V_C, P_C) = 0 \quad (4.26)$$

with some other function f_2 .

3. The zeroth law states that Eqs. (4.24) and (4.26) imply a third relation of the form

$$f_3(V_A, P_A, V_B, P_B) = 0 \quad (4.27)$$

for *all* values of the thermodynamic variables.

This is a little strange: If the equations were of the sort $f_1(V_A, P_A, x) = 0$ and $f_2(V_B, P_B, x) = 0$, then we could solve the first equation for $x = x_0(V_A, P_A)$ and insert this into the second equation to obtain $f_3(V_A, P_A, V_B, P_B) = f_2(V_B, P_B, x_0(V_A, P_A)) = 0$. In the present case, however, we have *two* variables V_C, P_C , but only one equation $f_1 = 0$, so we can naively only eliminate one of the two variables. The implication (4.24,4.26) \Rightarrow (4.27) can only be true if there is an A - and B -independent function

$$\tilde{T}_C(V_C, P_C) \quad (4.28)$$

such that

$$0 = f_1(V_A, P_A, V_C, P_C) = \hat{f}_1(V_A, P_A, \tilde{T}_C(V_C, P_C)), \quad (4.29)$$

$$0 = f_2(V_B, P_B, V_C, P_C) = \hat{f}_2(V_B, P_B, \tilde{T}_C(V_C, P_C)). \quad (4.30)$$

(The functions $f_{1,2}(\circ, \circ, \circ, \circ)$ have four arguments, $\hat{f}_{1,2}(\circ, \circ, \circ)$ have only three arguments.) We can then solve these two equations for \tilde{T}_C to obtain both

$$\tilde{T}_C(V_C, P_C) = \tilde{T}_A(V_A, P_A) \quad (4.31)$$

and

$$\tilde{T}_C(V_C, P_C) = \tilde{T}_B(V_B, P_B), \quad (4.32)$$

where we introduced two new functions $\tilde{T}_{A,B}$. This yields the desired formula

$$\tilde{T}_A(V_A, P_A) = \tilde{T}_B(V_B, P_B) \Rightarrow f_3(V_A, P_A, V_B, P_B) := \tilde{T}_A(V_A, P_A) - \tilde{T}_B(V_B, P_B) = 0 \quad (4.33)$$

4. The three systems in thermal equilibrium all have the same value of

$$\tilde{T} := \tilde{T}_A(V_A, P_A) = \tilde{T}_B(V_B, P_B) = \tilde{T}_C(V_C, P_C). \quad (4.34)$$

This defines both the empiric temperature and the equations of state for systems A, B, C .

Comment 1. If we use an ideal gas thermometer in this construction as C , then

$$\tilde{T} = \tilde{T}_C(V, P) = \frac{PV}{Nk_B} = T, \quad (4.35)$$

which agrees with the absolute temperature.

Comment 2. The derivation remains valid if the systems depend on more than the two variables V, P , say, N_1, N_2, \dots for mixtures. The equation of state obtained would be of the form

$$\tilde{T} = \tilde{T}_A(P, V, N_1, N_2, \dots). \quad (4.36)$$

Note that the particle number N that we tend to ignore falls into this category.

Comment 3. The zeroth law is proven fairly easily within the framework of statistical mechanics, where T is defined through $T^{-1} = \frac{\partial S}{\partial E}|_{V,N}$. Thermal equilibrium of A and C implies $T_A = T_C$ and that of B with C implies $T_B = T_C$. This implies $T_A = T_B$.

4.6 Absolute temperature

The zeroth law of thermodynamics implies the existence of *empirical temperature scales* such as the column length of a mercury thermometer. In principle, there are as many empiric temperatures as there are substances. We pick any such empiric temperature scale and denote it by \tilde{T} in the following. Another empirical temperature is the scale defined by an ideal gas thermometer, i.e. the temperature T defined through

$$T = \frac{PV}{Nk_B} \quad (4.37)$$

for an ideal gas. The two empirical temperatures can be converted into each other through calibration of thermometers, i.e. there is a function $T = T(\tilde{T})$ and its inverse.

In this section, we show that the findings on heat engines imply the existence of an absolute thermodynamic temperature scale, denoted ϑ , that is *intrinsic to thermodynamics* and thus *independent of the special properties of any thermodynamic substance*. All thermodynamic laws take on a simple form when this temperature scale is used. We will show that it coincides, up to an arbitrary constant factor a , with the ideal gas temperature scale, i.e.

$$\vartheta(\tilde{T}) = a \cdot T(\tilde{T}), \quad (4.38)$$

or, since \tilde{T} was arbitrary,

$$\vartheta = aT. \quad (4.39)$$

We then choose $a = 1$ by convention and arrive at

$$\vartheta = T. \quad (4.40)$$

We start from statement B that for all *reversible* engines operating between (empirical) temperatures \tilde{T}_1 and \tilde{T}_2 , the ratio Q_2/Q_1 is identical. Thus

$$\left(\frac{Q_2}{Q_1}\right)_{\text{rev}} = f(\tilde{T}_2, \tilde{T}_1) \quad (4.41)$$

for one cycle, with some fundamental function $f(\circ, \circ)$. Choose an *arbitrary* small temperature \tilde{T}_0 such that

$$\tilde{T}_0 < \tilde{T}_1 < \tilde{T}_2 \quad (4.42)$$

and three corresponding heat sources "0", "1", and "2". We consider two more reversible engines, En_1 and En_2 . During one cycle, engine En_1 extracts the amount of heat Q_1 from "1" and releases the amount of heat Q_0 into "0". We have

$$\left(\frac{Q_1}{Q_0}\right)_{\text{rev}} = f(\tilde{T}_1, \tilde{T}_0). \quad (4.43)$$

In contrast, engine En_2 extracts the amount of heat Q_2 from "2" and releases Q_0 into "0". We have

$$\left(\frac{Q_2}{Q_0}\right)_{\text{rev}} = f(\tilde{T}_2, \tilde{T}_0). \quad (4.44)$$

Taking the ratio of these two equations we conclude

$$f(\tilde{T}_2, \tilde{T}_1) = \frac{f(\tilde{T}_2, \tilde{T}_0)}{f(\tilde{T}_1, \tilde{T}_0)}. \quad (4.45)$$

(More accurately, we would have to consider the combined process of running one cycle of engine En_2 followed by one cycle of the reversed engine En_1 . The outcome is the same.) Since \tilde{T}_0 was arbitrary, we may keep it constant in all our equations. Hence we regard $f(\tilde{T}, \tilde{T}_0)$ as a function of \tilde{T} alone. We define a new temperature scale

$$\vartheta(\tilde{T}) = bf(\tilde{T}, \tilde{T}_0) \quad (4.46)$$

with some constant b . We then arrive at

$$\left(\frac{Q_2}{Q_1}\right)_{\text{rev}} = \frac{\vartheta(\tilde{T}_2)}{\vartheta(\tilde{T}_1)} = \frac{\vartheta_2}{\vartheta_1}. \quad (4.47)$$

for all reversible cycles. The temperature scale defined by the variable ϑ is called the *absolute thermodynamic temperature scale*. We are free to choose the unit of this scale, since only ratios appear in this equation. The usual choice is made by setting the difference between the boiling temperature and freezing temperature of water at atmospheric pressure to be 100 units (#).

We finally show that $\vartheta = aT$ by computing Q_2/Q_1 for the Carnot process of an ideal gas, which is a reversible process. The outcome is

$$\left(\frac{Q_2}{Q_1}\right)_{\text{Carnot}} = \frac{T_2}{T_1} \Rightarrow \vartheta = aT, \quad (4.48)$$

with an arbitrary scale factor a . The way we have chosen the units for ϑ in (#), however, implies $a = 1$.

For the computation of Q_2/Q_1 for the Carnot process we consider an ideal gas with heat capacity ratio κ . The work done along the isothermal lines is

$$L_{A \rightarrow B} = Nk_B T_2 \ln\left(\frac{V_B}{V_A}\right) > 0, \quad (4.49)$$

$$L_{C \rightarrow D} = -Nk_B T_1 \ln\left(\frac{V_C}{V_D}\right) < 0. \quad (4.50)$$

No heat is absorbed along the adiabatic lines and we have

$$Q_2 = Q_{A \rightarrow B} > 0, \quad (4.51)$$

$$-Q_1 = Q_{C \rightarrow D} < 0. \quad (4.52)$$

Now now use that the operating substance is an ideal gas and so the energy $E(V, T) = E(T)$ only depends on the temperature. Thus points along isotherms have the same energy,

$$E_A = E_B, \quad (4.53)$$

$$E_C = E_D. \quad (4.54)$$

This implies that work equals heat along the isothermal lines,

$$Q_2 = L_{A \rightarrow B} = Nk_B T_2 \ln\left(\frac{V_B}{V_A}\right) > 0, \quad (4.55)$$

$$Q_1 = -L_{C \rightarrow D} = Nk_B T_1 \ln\left(\frac{V_C}{V_D}\right) > 0. \quad (4.56)$$

To relate the volumes, we use that along the adiabatic lines we have $TV^{\kappa-1} = \text{const}$ so that

$$\frac{T_2}{T_1} = \left(\frac{V_C}{V_B}\right)^{\kappa-1} = \left(\frac{V_D}{V_A}\right)^{\kappa-1} \Rightarrow \frac{V_C}{V_D} = \frac{V_B}{V_A}. \quad (4.57)$$

For the heat ratio we eventually obtain

$$\frac{Q_2}{Q_1} = \frac{T_2 \ln\left(\frac{V_B}{V_A}\right)}{T_1 \ln\left(\frac{V_C}{V_D}\right)} = \frac{T_2}{T_1}. \quad (4.58)$$

This concludes the derivation of $\vartheta = T$.

4.7 Clausius inequality

We consider a system \mathcal{S} that undergoes a cyclic transformation. We suppose that during the cycle the system receives heat from or surrenders heat to a set of n heat sources having temperatures T_1, T_2, \dots, T_n . Denote the amounts of heat exchanged between the system and the sources by Q_1, Q_2, \dots, Q_n . We take Q_i positive if heat is received by the system and negative in the other case.

We prove that

$$\sum_{i=1}^n \frac{Q_i}{T_i} \leq 0. \quad (4.59)$$

(Clausius inequality)

The equality sign holds if the cycle is reversible.

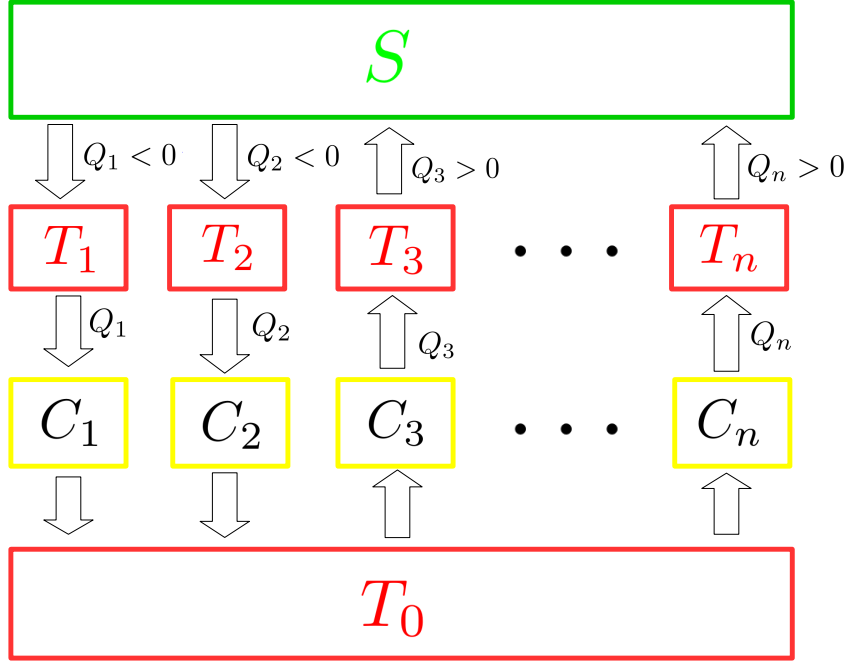


Figure 4.4: Combined cycle used in the proof of Clausius's inequality

Example. Let us consider the case of heat engines operating between two sources with T_1 and T_2 , i.e. $n = 2$. We have shown that

$$\frac{T_2}{T_1} = \left(\frac{Q_2}{|Q_1|} \right)_{\text{rev}} \geq \frac{Q_2}{|Q_1|}. \quad (4.60)$$

Note that $Q_1 = -|Q_1| < 0$ with the sign convention used here. This implies

$$T_2|Q_1| \geq T_1Q_2 \Leftrightarrow 0 \geq T_1Q_2 - T_2|Q_1| = T_1Q_2 + T_2Q_1. \quad (4.61)$$

Dividing by T_1T_2 we obtain

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leq 0 \quad (4.62)$$

as claimed. The same derivation also shows that equality holds for reversible cycles.

Proof. Consider an additional heat source "0" at an arbitrary temperature T_0 . Between the source at T_0 and each of the n heat sources at T_i we insert a reversible Carnot engine C_i . The Carnot engine C_i is such that if the system receives (surrenders) the amount of heat $|Q_i|$ to the source "i", then C_i surrenders (receives) the amount of heat $|Q_i|$ to the source "i". So if Q_i is the heat absorbed by the system at T_i , then $-Q_i$ is the heat absorbed by the Carnot engines at T_i . After running the combined cycle of S followed by C_1, \dots, C_n , the n heat sources remain unchanged.

Each Carnot engine C_i , schematically, is a heat engine that receives a positive amount of heat $Q^{(a)} > 0$ at $T^{(a)}$ and releases a positive amount of heat $Q^{(b)} > 0$ at $T^{(b)}$, with

$$\frac{Q^{(a)}}{Q^{(b)}} = \frac{T^{(a)}}{T^{(b)}}. \quad (4.63)$$

In this case, $|Q_i|$ at T_i is one of the positive numbers. The other, $|Q_{i,0}|$, is the amount of heat exchanged between \mathcal{C}_i and the heat source "0". Thus

$$|Q_{i,0}| = \frac{T_0}{T_i} |Q_i|. \quad (4.64)$$

Denote by $Q_{i,0}$ the amount of heat absorbed by \mathcal{C}_i from "0". If $Q_i > 0$ (system receives heat at T_i and \mathcal{C}_i releases heat at T_i), then $Q_{i,0} > 0$. If $Q_i < 0$ (system releases heat at T_i and \mathcal{C}_i receives heat at T_i), then $Q_{i,0} < 0$. Thus Q_i and $Q_{i,0}$ have the same sign,

$$Q_{i,0} = \frac{T_0}{T_i} Q_i. \quad (4.65)$$

Now we run the combined cycle of \mathcal{S} followed by $\mathcal{C}_1, \dots, \mathcal{C}_n$. The source at T_0 surrenders a total amount of heat

$$Q_0 = \sum_{i=1}^n Q_{i,0} = T_0 \sum_{i=1}^n \frac{Q_i}{T_i} \quad (4.66)$$

to the Carnot engines. Since the total system consisting of $\mathcal{S}, \mathcal{C}_1, \dots, \mathcal{C}_n$ returns to its initial state, the 1st law for cyclic processes applies, and the amount of heat Q_0 is converted into work done given by $L = Q_0$. Since this is the only final result of the cycle (the heat sources at T_1, \dots, T_n remain unchanged), we conclude that $L \leq 0$, since otherwise Kelvin's statement would be violated. Hence $Q_0 \leq 0$, or

$$\sum_{i=1}^n \frac{Q_i}{T_i} \leq 0. \quad (4.67)$$

If the cycle is performed reversible, we can run it in the reversed direction, which means that all Q_i change sign (but Q_0 does not). We then have

$$\sum_{i=1}^n \left(-\frac{Q_i}{T_i} \right)_{\text{rev}} \leq 0, \quad (4.68)$$

which together with the Clausius inequality implies

$$\left(\sum_{i=1}^n \frac{Q_i}{T_i} \right)_{\text{rev}} = 0. \quad (4.69)$$

This completes the proof of the theorem. \square

We assumed that the number of sources at T_1, \dots, T_N is finite. It is important to also consider the case for which the system exchanges heat with a continuous distribution of sources. Denoting by \oint the integral extended over a cycle, say in the PV-diagram, and by dQ the infinitesimal amount of heat received by the system from a source at temperature T , we have

$$\oint \frac{dQ}{T} \leq 0, \quad (4.70)$$

which is valid for all cycles, and

$$\oint \frac{dQ}{T} = 0, \quad (4.71)$$

which is valid only for reversible cycles.

Comment. Note that T in the denominator is the temperature of the source. This coincides with the system temperature for reversible cycles, where system and source are in equilibrium at each point. For irreversible processes, however, heat can only flow from hot to cold bodies, so the source is hotter for $dQ > 0$ or colder for $dQ < 0$.

4.8 Entropy

The Clausius (in)equality for reversible cycles reads

$$\oint_{\mathcal{C}} \frac{dQ}{T} = 0, \quad (4.72)$$

where \mathcal{C} is a reversible transformation, for instance a closed loop in the PV-diagram. Consider now two equilibrium states A and B of a system and some reversible transformation \mathcal{P}_{rev} that takes the system from A to B. The value of the integral

$$I_{A \rightarrow B} = \int_{\mathcal{P}_{\text{rev}}} \frac{dQ}{T} \quad (4.73)$$

is *independent of the reversible path chosen*. Indeed, if $\mathcal{P}'_{\text{rev}}$ is another reversible path connecting A and B, then we denote by $\mathcal{P}'_{\text{rev}}{}^{-1}$ the reversed path connecting B and A. We have

$$I'_{A \rightarrow B} = \int_{\mathcal{P}'_{\text{rev}}} \frac{dQ}{T} \quad (4.74)$$

and

$$I'_{B \rightarrow A} = \int_{\mathcal{P}'_{\text{rev}}{}^{-1}} \frac{dQ}{T} = - \int_{\mathcal{P}'_{\text{rev}}} \frac{dQ}{T} = -I'_{A \rightarrow B}. \quad (4.75)$$

(This is true for any line-integral: Going along the path in one or the other direction gives an overall minus sign.) Consider now the combined reversible transformation $\mathcal{C} = \mathcal{P}_{\text{rev}} \cup \mathcal{P}'_{\text{rev}}{}^{-1}$. This is a reversible cycle and

$$\begin{aligned} 0 &= \oint_{\mathcal{C}} \frac{dQ}{T} \\ &= \int_{\mathcal{P}_{\text{rev}}} \frac{dQ}{T} + \int_{\mathcal{P}'_{\text{rev}}{}^{-1}} \frac{dQ}{T} \\ &= I_{A \rightarrow B} + I'_{B \rightarrow A} \\ &= I_{A \rightarrow B} - I'_{A \rightarrow B}. \end{aligned} \quad (4.76)$$

This proof our claim.

Entropy. The property just shown allows us to define a new function of state of the system, the entropy. It is one of the most important quantities in thermodynamics and, in fact, most areas of physics. We choose an arbitrary equilibrium state O of our system. For any other equilibrium state A we define the *entropy of state A* as

$$S_A = \int_O^A \frac{dQ}{T}, \quad (4.77)$$

where the path connecting O and A is taken to be reversible. We have seen that the value of S_A is independent of the reversible path chosen. Since the path is reversible, its initial and final points must be equilibrium states. Consequently, S_A is only defined for equilibrium states A . If we choose another equilibrium state B , then

$$S_B = \int_O^B \frac{dQ}{T} \quad (4.78)$$

along some reversible path connecting O and B . Since we have

$$\int_O^A \frac{dQ}{T} = - \int_A^O \frac{dQ}{T}, \quad (4.79)$$

this implies that the entropy difference between states A and B is given by

$$S_B - S_A = \int_O^B \frac{dQ}{T} - \int_O^A \frac{dQ}{T} = \int_A^O \frac{dQ}{T} + \int_O^B \frac{dQ}{T} = \int_A^B \frac{dQ}{T}, \quad (4.80)$$

where any reversible path connecting A and B can be chosen. For an infinitesimal reversible transformation we have

$$dQ = TdS \text{ (reversible)}. \quad (4.81)$$

In the context of differentials introduced in Section 3.3, the heat dQ is not an exact differential and $\int_A^B dQ$ depends on the path. In contrast, the entropy

$$dS = \frac{1}{T}dQ \text{ (reversible)} \quad (4.82)$$

is an exact differential and

$$\int_A^B dS = S_B - S_A \quad (4.83)$$

is independent of the reversible path chosen to connect A and B . Similarly, the work dL is not an exact differential and $\int_A^B dL$ depends on the path, but the volume

$$dV = \frac{1}{P}dL \text{ (reversible)} \quad (4.84)$$

is an exact differential and

$$\int_A^B dV = V_B - V_A \quad (4.85)$$

is independent of the reversible path chosen to connect A and B . One might say that the existence of the function of state "entropy" restores a symmetry between work and heat in these equations.

Comment 1. The natural unit of entropy is k_B , because $Q \propto \text{J}$, $T \propto \text{K}$, so $S \propto \frac{\text{J}}{\text{K}} \propto k_B$.

Comment 2. The entropy is an extensive variable.

Some properties of the entropy. We show the following important properties of the entropy:

(1) The entropy of independent subsystems is additive. This implies that entropy is extensive.

(2) For *any* thermodynamic transformation connecting equilibrium states A and B we have

$$\Delta S = S_B - S_A \geq \int_A^B \frac{dQ}{T}, \quad (4.86)$$

where equality holds for reversible transformations.

(3) For a thermally isolated system, we have

$$S_B \geq S_A \quad (4.87)$$

for any transformation connecting A and B .

(4) For a thermally isolated system, entropy does not change during reversible transformations, $S_A = S_B$.

(5) For a thermally isolated system, the equilibrium state is the state of maximum entropy consistent with the external constraints.

For (1), we need to define what independent systems are. For this we assume that a thermodynamic system \mathcal{S} splits into several subsystems $\mathcal{S}_1, \dots, \mathcal{S}_n$ which are in equilibrium each (but not necessarily with each other). We say the subsystems are independent if they are so large that the energy of the total system can be split into the energies of the subsystems,

$$E = E_1 + \dots + E_n, \quad (4.88)$$

and the work done by the system in any transformation is equal to the work done by the subsystems,

$$W = W_1 + \dots + W_n. \quad (4.89)$$

We then have $Q = Q_1 + \dots + Q_n$ and entropy is additive according to

$$S = \int_O^A \frac{dQ}{T} = \int_O^A \frac{dQ_1}{T} + \dots + \int_O^A \frac{dQ_n}{T} = S_1 + \dots + S_n. \quad (4.90)$$

This allows us to define the entropy for certain non-equilibrium systems, for instance for inhomogeneous systems with spatially varying thermodynamic parameters. An example where $E \neq E_1 + \dots + E_n$ is, for instance, an interface between two substances that has a significant surface energy.

For (2), consider two equilibrium states A and B . Let \mathcal{P} be any transformation connecting A and B , and \mathcal{P}' be a reversible transformation connecting A and B . The transformation $\mathcal{C} = \mathcal{P} \cup \mathcal{P}'^{-1}$ is a cycle and we have

$$0 \geq \oint_{\mathcal{C}} \frac{dQ}{T} \quad (4.91)$$

$$= \int_{\mathcal{P}} \frac{dQ}{T} + \int_{\mathcal{P}'^{-1}} \frac{dQ}{T} \quad (4.92)$$

$$= \int_{\mathcal{P}} \frac{dQ}{T} - \int_{\mathcal{P}'} \frac{dQ}{T} \quad (4.93)$$

$$= \int_{\mathcal{P}} \frac{dQ}{T} - [S_B - S_A], \quad (4.94)$$

thus

$$S_B - S_A \geq \int_{\mathcal{P}} \frac{dQ}{T} = \int_A^B \frac{dQ}{T} \quad (4.95)$$

as claimed.

For (3), consider a thermally isolated system. Since it cannot exchange heat with its environment we have

$dQ = 0$ and thus $S_B - S_A \geq 0$ as claimed.

For (4), use that "=" applies in (3) for reversible transformations.

For (5), consider a thermally isolated system subject to some external constraints such as fixed volume V . The system may be in one of many (possibly inhomogeneous) thermodynamic states that satisfy these constraints.² If the system is not in equilibrium, due to the microscopic motion of atoms or molecules, it will, over time, undergo spontaneous thermodynamic processes that slightly change its thermodynamic state. Any such transformation, however, needs to satisfy $\Delta S \geq 0$ according to (3). Consequently, if we wait long enough for the time-independent equilibrium state to set in, then this state must be a state of maximum entropy.

Comment 1. The entropy of a system *can* decrease in a thermodynamic transformation. This requires that the system is not thermally isolated from its environment, which is often the case. However, if the environment and the system together are thermally isolated from the rest of the universe, then the entropy of the combined system cannot decrease.

Comment 2. From (4) and (5) it follows that the approach to equilibrium is an irreversible process. This is intuitively clear.

Example 1. Reversible isothermal expansion of an ideal gas. Assume the volume increases from V_A to V_B . Since T does not change and $E = E(T)$, we have $\Delta E = 0$ and

$$Q = L = Nk_B T \ln \frac{V_B}{V_A}. \quad (4.96)$$

Consequently, for the system,

$$\Delta S_{\text{sys}} = \int_A^B \frac{dQ}{T} = \frac{1}{T} \int_A^B dQ = \frac{Q}{T} = Nk_B \ln \frac{V_B}{V_A}. \quad (4.97)$$

The heat Q is supplied by the environment and we have

$$\Delta S_{\text{env}} = -\frac{Q}{T} = -Nk_B \ln \frac{V_B}{V_A}, \quad (4.98)$$

so that

$$\Delta S_{\text{sys}} + \Delta S_{\text{env}} = 0. \quad (4.99)$$

Example 2. Free isothermal expansion of an ideal gas. This is an irreversible process. As we have seen in the section on heat capacity and calorimeters, no heat is supplied by the environment and no work is done, $Q = W = 0$. We may naively assume that $Q = 0$ implies $\Delta S \sim \int \frac{dQ}{T} = 0$, but this is *wrong*. Indeed, we can only conclude that

$$\Delta S_{\text{sys}} \geq \int_A^B \frac{dQ}{T} = 0, \quad (4.100)$$

²The typical example is a gas that occupies only one half-space of a room: a clear non-equilibrium state, although consistent with external constraints.

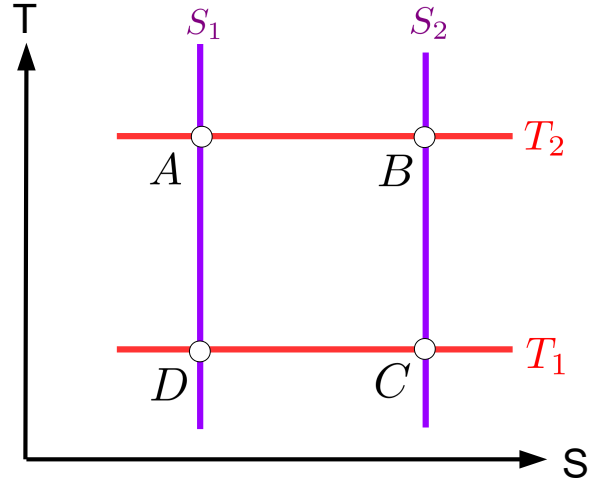


Figure 4.5: Carnot cycle in the TS-diagram

which does not rule out $\Delta S \neq 0$. In fact, since entropy is a function of state and the initial and final states, A and B , are the same equilibrium states for both the reversible and free expansion, we have

$$\Delta S_{\text{sys}} = S_B - S_A = Nk_B \ln \frac{V_B}{V_A} \quad (4.101)$$

in both cases. The free expansion is thus an example of a process with $dQ = 0$, but $dS \neq 0$. This is no contradiction since we only have $dQ = TdS$ for reversible processes. For the free expansion, however, we have

$$\Delta S_{\text{env}} = 0 \quad (4.102)$$

for the environment, as it does not participate in the transformation, and so

$$\Delta S_{\text{sys}} + \Delta S_{\text{env}} = Nk_B \ln \frac{V_B}{V_A} > 0. \quad (4.103)$$

Carnot cycle in the TS-diagram. It is instructive to study the reversible Carnot cycle in the TS-diagram, instead of the PV-diagram. During the adiabatic transformations $B \rightarrow C$ and $D \rightarrow A$, we have $dQ = 0$, and thus $dS = 0$. These correspond to vertical lines in the TS-diagram. The isothermal lines $A \rightarrow B$ and $C \rightarrow D$ are horizontal lines. The net amount of heat extracted from the environment, due to $dQ = TdS$ in reversible processes, is given by the area under the curve. We have

$$L = Q_2 - Q_1 = Q_{\text{net}} = (T_2 - T_1)(S_2 - S_1). \quad (4.104)$$

Furthermore,

$$Q_2 = T_2(S_2 - S_1), \quad (4.105)$$

so that

$$\eta = \frac{L}{Q_2} = 1 - \frac{T_1}{T_2}. \quad (4.106)$$

Differentials of energy and entropy. Consider a state in thermodynamic equilibrium, represented, for instance, by a point in the PV-diagram. Choose any infinitesimally close equilibrium state and a reversible transformation connecting them. The first law of thermodynamics then reads

$$dE = dQ + dW = TdS - PdV. \quad (4.107)$$

Recall that we read this as

$$T = \left(\frac{\partial E}{\partial S}\right)_V, \quad P = -\left(\frac{\partial E}{\partial V}\right)_S. \quad (4.108)$$

Equivalently,

$$dS = \frac{1}{T}dE + \frac{P}{T}dV, \quad (4.109)$$

hence

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V, \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_E. \quad (4.110)$$

These relations are true for any thermodynamic equilibrium state.

5 Thermodynamics potentials

5.1 Free energy

In this section, we consider a system that is in thermal contact with a heat bath (environment) of constant temperature T . Work W may be performed on the system. We also assume for simplicity that the system is homogeneous.

Thermal equilibrium. Assume the system with energy E and entropy S is in thermal equilibrium with the heat bath at T , so that the system also has temperature T . We define the *free energy* by

$$F = E - TS. \quad (5.1)$$

The free energy is a function of state, since E, T, S are functions of state. Consider now a thermodynamic transformation from state A to state B and define

$$\Delta F = F_B - F_A. \quad (5.2)$$

We show that:

The work done during the transformation satisfies

$$L \leq -\Delta F, \quad (5.3)$$

or, perhaps more memorably,

$$L_{\max} = -\Delta F. \quad (5.4)$$

Equality holds for reversible transformations. In words: For a system in thermal equilibrium with a heat bath at constant temperature, the work done during a reversible transformation is equal to the decrease in free energy of the system.

For the proof, recall that

$$\int_A^B \frac{dQ}{T} \leq S_B - S_A, \quad (5.5)$$

where equality holds for reversible transformations. Since the temperature of the bath T is constant during the transformation, we have

$$Q = \int_A^B dQ \leq T(S_B - S_A). \quad (5.6)$$

From the first law of thermodynamics we have

$$L = -\Delta E + Q \quad (5.7)$$

$$\leq E_A - E_B + T(S_B - S_A) \quad (5.8)$$

$$= [E_A - TS_A] - [E_B - TS_B] \quad (5.9)$$

$$= F_A - F_B \quad (5.10)$$

$$= -\Delta F. \quad \square \quad (5.11)$$

Thermal contact only. If the system is not in thermal equilibrium with the bath, but rather in a state A of temperature T_A , then the free energy of the system is

$$F_A = E - T_A S, \quad (5.12)$$

or, more precise,

$$F_A = E_A - T_A S_A. \quad (5.13)$$

For any thermodynamic transformation from A to B (with temperatures T_A and T_B) when coupled to a heat bath at temperature T , the above derivation yields

$$L_{\max} = [E_A - T S_A] - [E_B - T S_B], \quad (5.14)$$

but the right-hand side no longer coincides with $-\Delta F$.

Consider now a system in thermal contact with a heat bath at constant temperature T such that the environment cannot perform work on the system,

$$W = 0. \quad (5.15)$$

For homogeneous systems, this reduces to constant volume, V . For any thermodynamic transformation between states A and B of the system we have

$$F_B \leq F_A, \quad (5.16)$$

or,

$$\Delta F \leq 0. \quad (5.17)$$

Consequently, the free energy cannot increase during any transformation and *the equilibrium state is the state of minimum free energy*. The value of the equilibrium free energy, F_{eq} , is fully determined by the thermodynamic variables of the system, here T and V , so that

$$F_{\text{eq}}(T, V) = F_{\min}. \quad (5.18)$$

This condition is not unlike for purely mechanical systems with kinetic and potential energy given by $\frac{m}{2}\dot{x}^2 + U(x)$, where the stable configuration is a time-independent solution that minimizes the potential energy $U(x)$. The free energy plays a role akin to the potential energy in classical mechanics, but for thermodynamic systems in contact with a heat source.

Digression: Product rule for differentials. Consider two functions $f(x)$ and $g(x)$ of one variable. The product rule of differentiation states that

$$\frac{d}{dx} [f(x)g(x)] = f'(x)g(x) + f(x)g'(x) \quad (5.19)$$

$$= \frac{df}{dx}g + f\frac{dg}{dx}. \quad (5.20)$$

Multiplying by dx we obtain

$$d(fg) = g df + f dg. \quad (5.21)$$

This simple equation is of great importance in thermodynamics!

To see why, recall that for reversible transformations we have

$$dE = TdS - PdV. \quad (5.22)$$

Consequently,

$$dF = d(E - TS) \quad (5.23)$$

$$= dE - TdS - SdT \quad (5.24)$$

$$= [TdS - PdV] - TdS - SdT \quad (5.25)$$

$$= -SdT - PdV. \quad (5.26)$$

Analogous to our analysis of dE and dS , we conclude that for any thermodynamic equilibrium state we have

$$dF = -SdT - PdV, \quad (5.27)$$

which implies

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad P = -\left(\frac{\partial F}{\partial V}\right)_T. \quad (5.28)$$

5.2 Chemical potential

So far we have mostly considered the case of constant particle number N . However, in many physical processes, the particle number can change because the system exchanges particles with the environment. Examples:

- Chemical reactions, like $2\text{H} + \text{O} \rightleftharpoons \text{H}_2\text{O}$. The number N of water molecules varies in time. In equilibrium, a certain number N_{eq} is realized.
- Gas molecules adsorbed on a solid or liquid surface (system) surrounded by the gas (environment). Gas molecules permanently attach or detach from the surface, so the number of adsorbed particles N varies in time. In equilibrium, a certain number N_{eq} is realized.
- Two differently colored liquids separated by a permeable membrane, for instance a coffee filter. The number of particles of each color, N_1 and N_2 , on either side of the membrane vary in time.

In the following, if a system can exchange particles with its environment, we say that they are in *chemical contact*. If we wait long enough so that the particle number of the system N does not change and reached its equilibrium value N_{eq} , we say that the system and environment are in *chemical equilibrium*.

We define the *chemical potential* as

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}. \quad (5.29)$$

The differential of the energy becomes

$$dE = TdS - PdV + \mu dN. \quad (5.30)$$

This replaces the infinitesimal form of the 1st law of thermodynamics if N is not constant during a thermodynamic transformation. Since E and S are extensive, we find that μ is intensive.

We have the following three sets of extensive and intensive thermodynamic variables:

category	extensive	intensive
thermal	S	T
mechanical	V	P
chemical	N	μ

They always show up in these pairs in thermodynamic differentials. For instance, for the entropy S and free energy $F = E - TS$ we have

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN, \quad (5.31)$$

$$dF = -SdT - PdV + \mu dN. \quad (5.32)$$

Exercise: Show these starting from dE .

Interpretation. What does the chemical potential mean or measure? The definition of μ implies that it is measured in units of energy, say, Joule. It amounts to the energy costs ΔE when adding one particle to the system at constant S and V , or the free energy cost ΔF when adding a particle at constant T and V . Another perhaps more useful interpretation is to think of μ simply as some parameter which is such that if μ increases, the particle number N increases. Similarly, the temperature T is some parameter such that if T increases, the energy increases.

If two systems “1” and “2” are in thermal and mechanical equilibrium, then their temperatures $T_{1,2}$ and pressures $P_{1,2}$ satisfy

$$\text{thermal equilibrium: } T_1 = T_2, \quad (5.33)$$

$$\text{mechanical equilibrium: } P_1 = P_2. \quad (5.34)$$

$$(5.35)$$

Similarly, if they are in chemical equilibrium, their chemical potentials $\mu_{1,2}$ satisfy

$$\text{chemical equilibrium: } \mu_1 = \mu_2. \quad (5.36)$$

$$(5.37)$$

This can be derived as follows: Consider the combined system “1+2” and isolate it (thermally, mechanically, and chemically) from any other system. Then other systems cannot exchange heat or particles with the system or do work on it. As a result, energy E , volume V , and particle number N of the combined system are constant in time. However, it is not fixed how the total energy, volume, particle number divides among the two parts “1” and “2” of the system. We have

$$E = E_1 + E_2, \quad (5.38)$$

$$V = V_1 + V_2, \quad (5.39)$$

$$N = N_1 + N_2. \quad (5.40)$$

The total entropy $S(E, V, N)$ is additive, so

$$S(E, V, N) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2) \quad (5.41)$$

$$= S_1(E_1, V_1, N_1) + S_2(E - E_1, V - V_1, N - N_1). \quad (5.42)$$

In equilibrium, the numbers E_1 , V_1 , and N_1 will be such that the entropy of the combined system is maximal. (The numbers $E_2 = E - E_1$, $V_2 = V - V_1$, $N_2 = N - N_1$ are then automatically determined by the values of E, V, N .) We denote these values by the subscript “eq” for equilibrium. This means that the function $S(E, V, N)$ is maximal with respect to the free, independent parameters E_1, V_1, N_1 . The first derivatives vanish at the maximum, hence

$$0 \stackrel{!}{=} \left. \frac{\partial S}{\partial E_1} \right|_{\text{eq}} = \left. \frac{\partial S_1}{\partial E_1} \right|_{\text{eq}} - \left. \frac{\partial S_2}{\partial E_2} \right|_{\text{eq}} = \left(\frac{1}{T_1} - \frac{1}{T_2} \right)_{\text{eq}}, \quad (5.43)$$

$$0 \stackrel{!}{=} \left. \frac{\partial S}{\partial V_1} \right|_{\text{eq}} = \left. \frac{\partial S_1}{\partial V_1} \right|_{\text{eq}} - \left. \frac{\partial S_2}{\partial V_2} \right|_{\text{eq}} = \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right)_{\text{eq}}, \quad (5.44)$$

$$0 \stackrel{!}{=} \left. \frac{\partial S}{\partial N_1} \right|_{\text{eq}} = \left. \frac{\partial S_1}{\partial N_1} \right|_{\text{eq}} - \left. \frac{\partial S_2}{\partial N_2} \right|_{\text{eq}} = - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right)_{\text{eq}}. \quad (5.45)$$

This completes the proof. \square

Gibbs–Duhem relation. Consider a homogeneous system with entropy $S(E, N, V)$. If we double the system, then we double the energy, volume, and particle number. Since entropy is extensive, we have

$$S(2E, 2V, 2N) = 2S(E, V, N). \quad (5.46)$$

This can be seen as a special case of $S(E, V, N) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$ for “1”=“2”. More generally, resizing the system by a scale factor λ we have

$$S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N). \quad (5.47)$$

Taking a derivative with respect to λ and setting $\lambda = 1$ eventually, we find

$$S(E, V, N) = \left. \frac{\partial}{\partial \lambda} [\lambda S(E, V, N)] \right|_{\lambda=1} \quad (5.48)$$

$$= \left. \frac{\partial}{\partial \lambda} S(\lambda E, \lambda V, \lambda N) \right|_{\lambda=1} \quad (5.49)$$

$$= \left[\frac{\partial S}{\partial E} \frac{\partial(\lambda E)}{\partial \lambda} + \frac{\partial S}{\partial V} \frac{\partial(\lambda V)}{\partial \lambda} + \frac{\partial S}{\partial N} \frac{\partial(\lambda N)}{\partial \lambda} \right]_{\lambda=1} \quad (5.50)$$

$$= \frac{\partial S}{\partial E} E + \frac{\partial S}{\partial V} V + \frac{\partial S}{\partial N} N \quad (5.51)$$

$$= \frac{1}{T} E + \frac{P}{T} V - \frac{\mu}{T} N. \quad (5.52)$$

Consequently,

$$E = TS - PV + \mu N \quad (5.53)$$

$$\text{Gibbs–Duhem relation.} \quad (5.54)$$

This is a very useful relation. It is true for every homogeneous thermodynamic system. By taking a differential of this relation we obtain

$$dE = TdS + SdT - PdV - VdP + \mu dN + Nd\mu \quad (5.55)$$

$$= \underbrace{[TdS - PdV + \mu dN]}_{dE} + SdT - VdP + Nd\mu, \quad (5.56)$$

hence

$$dP = \frac{S}{V}dT + \frac{N}{V}d\mu \quad (5.57)$$

$$= sdT + nd\mu. \quad (5.58)$$

(Here $s = S/V$ is the entropy density.) This equation is very important: It tells us that the three intensive variables T, P, μ are not independent, meaning they cannot be varied independently of one another. This *thermodynamic constraint* is true for every homogeneous system and independent of the equation of state.

5.3 Overview of thermodynamic potentials

In the following we define the thermodynamic potentials. They all share these properties:

- (1) They are functions of state.
- (2) They are extensive.
- (3) They depend on three thermodynamic variables, one chosen from each of the three pairs (T, S) , (P, V) , (μ, N) . One of the variables must be extensive.
- (4) When the three corresponding variables are held fixed, the potential cannot change under any reversible transformation, and under irreversible transformations, the potentials only decrease.
- (5) As a result, when the three corresponding variables are fixed, the equilibrium state will be such that the thermodynamic potential is minimal.

The three variables in (3) are chosen to reflect the thermodynamic situation. For instance, for a system that is thermally isolated from its environment, we choose S , whereas for a system in thermal contact with an environment at temperature T , we choose T instead of S . The reason that (T, P, μ) are not allowed in (3) is that they are not independent variables, due to $dP = sdT + nd\mu$. Also, it would be impossible to construct an extensive thermodynamic potential by using intensive variables only. The total number of possible thermodynamic potentials is thus

$$2^3 - 1 = 7. \quad (5.59)$$

However, only five of them are used in practice. Here is an overview of them:

potential	formula	thermal contact to environment	mechanical contact to environment	chemical contact to environment	equilibrium state
energy $E(S, V, N)$		×	×	×	minimal $E(S, V, N)$
free energy $F(T, V, N)$	$F = E - TS$	✓	×	×	minimal $F(T, V, N)$
enthalpy $H(S, P, N)$	$H = E + PV$	×	✓	×	minimal $H(S, P, N)$
free enthalpy $G(T, P, N)$	$G = F + PV$	✓	✓	×	minimal $G(T, P, N)$
grand potential $\Phi(T, V, \mu)$	$\Phi = F - \mu N$	✓	×	✓	minimal $\Phi(T, V, \mu)$

The potential $F(T, V, N)$ is also called Helmholtz free energy, the potential $G(T, P, N)$ is also called Gibbs free energy³. The name “grand potential” of $\Phi(T, V, \mu)$ derives from the fact that it naturally appears in the so-called grand-canonical ensemble in statistical mechanics. Obviously, we did not use the variable combinations (S, V, μ) and (S, P, μ) .⁴

³In Fermi’s book, G is called Φ .

⁴The relations between the thermodynamic potentials are so-called Legendre transformations, see my lecture notes for PHYS 530, section 3.2.

The differentials of the thermodynamic potentials (valid for reversible transformations) read

$$dE = TdS - PdV + \mu dN, \quad (5.60)$$

$$dF = -SdT - PdV + \mu dN, \quad (5.61)$$

$$dH = TdS + VdP + \mu dN, \quad (5.62)$$

$$dG = -SdT + VdP + \mu dN, \quad (5.63)$$

$$d\Phi = -SdT - PdV - Nd\mu. \quad (5.64)$$

For instance,

$$dH = d(E + PV) \quad (5.65)$$

$$= dE + PdV + VdP \quad (5.66)$$

$$= [TdS - PdV + \mu dN] + PdV + VdP \quad (5.67)$$

$$= TdS + VdP + \mu dN. \quad (5.68)$$

Exercise: Show the remaining ones.

The grand potential must have the form

$$\Phi(T, V, \mu) = V\varphi(T, \mu) \quad (5.69)$$

with some function $\varphi(\cdot, \cdot)$, because V is the only extensive variables and Φ must be extensive. However, the differential tells us that

$$\varphi(T, \mu) = \left(\frac{\partial \Phi}{\partial V} \right)_{T, \mu} = -P, \quad (5.70)$$

and so

$$\Phi = -PV. \quad (5.71)$$

This also follows from the Gibbs–Duhem relation $E = TS - PV + \mu N$, because

$$\Phi = F - \mu N \quad (5.72)$$

$$= E - TS - \mu N \quad (5.73)$$

$$= -PV. \quad (5.74)$$

This means that for system described by Φ , the equilibrium state is the state of maximal pressure $P(T, \mu)$.

The enthalpy $H(S, P, N)$ and free enthalpy $G(T, P, N)$ find applications in chemistry, because chemical reactions happening in a test tube are mostly performed at constant atmospheric pressure, not at fixed volume.

Equation of state. Specifying the equation of state of a system is equivalent to specifying its corresponding thermodynamic potential in the right variables, because all other thermodynamic parameters follow from derivatives of the thermodynamic potential.

Example 1. Consider a system with thermal and chemical contact to a bath, that is mechanically isolated. The equation of state is

$$\Phi(T, V, \mu) = -VP(T, \mu). \quad (5.75)$$

Indeed, we obtain all other thermodynamic functions from

$$S = -\left(\frac{\partial\Phi}{\partial T}\right)_{V,\mu}, \quad P = -\left(\frac{\partial\Phi}{\partial V}\right)_{T,\mu}, \quad N = -\left(\frac{\partial\Phi}{\partial\mu}\right)_{T,V} \quad (5.76)$$

and

$$E = TS - PV + \mu N. \quad (5.77)$$

To obtain E , we could also integrate $dE = TdS - PdV + \mu dN$, since we know everything on the right-hand side.

Example 2. Consider a system in thermal contact with a bath, that is mechanically and chemically isolated. The equation of state is

$$F(T, V, N). \quad (5.78)$$

From this we obtain

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \quad (5.79)$$

and

$$E = TS - PV + \mu N. \quad (5.80)$$

5.4 Maxwell relations

Consider an infinitesimal transformation that changes two parameters x, y by dx, dy and the expression

$$\delta(x, y) = a(x, y)dx + b(x, y)dy. \quad (5.81)$$

The following two properties of δ are equivalent.

(1)

$$\frac{\partial a}{\partial y} = \frac{\partial b}{\partial x} \quad (5.82)$$

(2) There exists a function of state R such that

$$\delta = dR = a dx + b dy \quad (5.83)$$

and, hence,

$$a = \left(\frac{\partial R}{\partial x}\right)_y, \quad b = \left(\frac{\partial R}{\partial y}\right)_x. \quad (5.84)$$

Furthermore, for a thermodynamic transformation from state A to B , the integral

$$\int_A^B dR = R_B - R_A \quad (5.85)$$

is independent of the path.

(We do not prove this here.) Property (1) is called the *integrability condition*. Expressed in terms of R , it

simply states that second derivatives can be exchanged,

$$\frac{\partial^2 R}{\partial x \partial y} = \frac{\partial^2 R}{\partial y \partial x}. \quad (5.86)$$

Property (2) is satisfied for all thermodynamic potentials, $R = E, F, \dots$, when considering reversible transformations. The variables x, y can be chosen to be any of the three variables of the potential while keeping the third one fixed. The equation (1) then yields quite nontrivial thermodynamic identities, called *Maxwell relations*.

For instance, choosing $R = F(T, V, N)$ and $x, y \in \{T, V, N\}$, there are

$$\binom{3}{2} = 3 \quad (5.87)$$

different relations to be obtained. We start from

$$dF = -SdT - PdV + \mu dN \quad (5.88)$$

and obtain the Maxwell relations

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V} \Rightarrow \left(\frac{\partial}{\partial V}(-S) = \frac{\partial}{\partial T}(-P) \right) \Rightarrow \left(\frac{\partial S}{\partial V} \right)_{T,N} = \left(\frac{\partial P}{\partial T} \right)_{V,N}, \quad (5.89)$$

$$\frac{\partial^2 F}{\partial N \partial T} = \frac{\partial^2 F}{\partial T \partial N} \Rightarrow \left(\frac{\partial}{\partial N}(-S) = \frac{\partial}{\partial T}(\mu) \right) \Rightarrow -\left(\frac{\partial S}{\partial N} \right)_{T,V} = \left(\frac{\partial \mu}{\partial T} \right)_{V,N}, \quad (5.90)$$

$$\frac{\partial^2 F}{\partial N \partial V} = \frac{\partial^2 F}{\partial V \partial N} \Rightarrow \left(\frac{\partial}{\partial N}(-P) = \frac{\partial}{\partial V}(\mu) \right) \Rightarrow -\left(\frac{\partial P}{\partial N} \right)_{T,V} = \left(\frac{\partial \mu}{\partial V} \right)_{T,N}. \quad (5.91)$$

The Maxwell relations are valid for every thermodynamic system. Using a different thermodynamic potential R , we get three different equations, since they necessarily differ in the set of variables. Not all of these equations may be equally useful in practice.

Example. Compressing a metal block. A typical application of Maxwell relations is to convert non-intuitive thermodynamic derivatives into so-called material constants, yielding useful formulas for experiment and engineering. As an example, consider a block of iron. Its specific properties are characterized by *material constants* such as heat capacities,

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_{V,N}, \quad (5.92)$$

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_{P,N}, \quad (5.93)$$

isothermal and adiabatic compressibilities,

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N}, \quad (5.94)$$

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{S,N}, \quad (5.95)$$

thermal expansion coefficient

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,N}, \quad (5.96)$$

or thermal pressure coefficient

$$\beta = \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_{V,N}. \quad (5.97)$$

(Careful: different authors use different labels.) These quantities can be measured and are tabulated for many materials. Assume now we compress the block of iron reversibly and at constant temperature from a pressure P_1 to a higher pressure $P_2 > P_1$. How much heat is released during this process? We have

$$dQ = TdS, \quad (5.98)$$

so we need dS . Using the thermodynamic independent variables T, P, N we have

$$dS = \left(\frac{\partial S}{\partial T} \right)_{P,N} dT + \left(\frac{\partial S}{\partial P} \right)_{T,N} dP + \left(\frac{\partial S}{\partial N} \right)_{T,P} dN. \quad (5.99)$$

Since $dT = dN = 0$, we have

$$dQ = T \left(\frac{\partial S}{\partial P} \right)_{T,N} dP. \quad (5.100)$$

We next use a Maxwell relation to rewrite the derivative. Since the variables T, P, N are involved, we might want to look at

$$dG = -SdT + VdP + \mu dN. \quad (5.101)$$

Indeed, this yields

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial^2 G}{\partial T \partial P} \Rightarrow \left(\frac{\partial}{\partial P} (-S) = \frac{\partial}{\partial T} (V) \right) \Rightarrow \left(\frac{\partial S}{\partial P} \right)_{T,N} = - \left(\frac{\partial V}{\partial T} \right)_{P,N} = -V\alpha. \quad (5.102)$$

Consequently,

$$dQ = -TV\alpha dP \quad (5.103)$$

and

$$Q = -T\alpha \int_{P_1}^{P_2} V dP. \quad (5.104)$$

Since the volume of the metal block will not change much when compressed, we can assume $V \approx \text{const}$ and so arrive at

$$Q = -TV\alpha(P_2 - P_1). \quad (5.105)$$

Heat is released from the body, so $Q < 0$.

Comment. The material constants are not all independent. For instance, using thermodynamic (but not Maxwell) relations, one can show that

$$\frac{C_V}{C_P} = \frac{\kappa_S}{\kappa_T} \quad (5.106)$$

for any substance.

5.5 Phase transitions

Definition of a phase. When a system consists of only a single homogeneous substance, it is said to consist of only one *phase*. If a heterogeneous system is composed of several parts, each of which is homogeneous in itself, the system is said to consist of several phases.

Comment. The important property of each part that comprises a phase is the spatial homogeneity. They can by themselves be mixtures of several chemical compounds, see the examples.

Examples. Systems composed of only one phase:

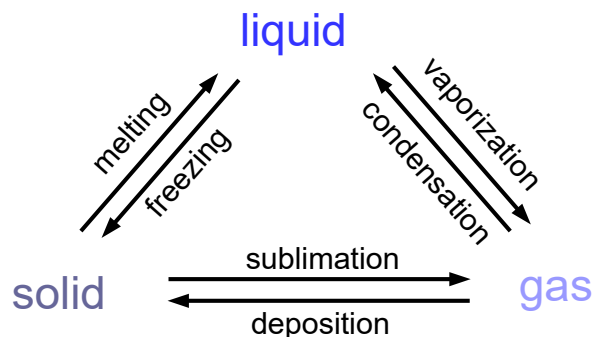
- (1) a homogeneous liquid (not necessarily a chemically pure substance: solutions may also be considered, for instance a homogeneous salt-water solution)
- (2) a homogeneous solid
- (3) a homogeneous gas

Systems that consist of two phases:

- (4) an ice block floating in water (phase 1: solid ice, phase 2: liquid water)
- (5) a system composed of water and water vapor (phase 1: liquid water, phase 2: gaseous vapor)
- (6) a saturated solution of salt in water with some of the solid salt present (phase 1: liquid salt-water solution, phase 2: solid salt)
- (7) a system composed of two immiscible liquids, for instance oil on top of water (phase 1: liquid 1, phase 2: liquid 2)

The thermodynamic properties of different phases are often quite distinctive, which allows us to tell them apart macroscopically. For instance, n is much higher for solids than for liquids or gases, or whereas $c_P \approx c_V$ for solids and liquids, we have $c_P > c_V$ for gases.

Assume a system is in one phase. If this system changes its phase through an external change of thermodynamic variables, it is said to undergo a *phase transition*. Some common phase transitions are:



If a system consists of two or more phases, we say that these phases *coexist*. The coexistence of phases is not generic in equilibrium, but rather requires special thermodynamic parameters; most systems are in one phase. In fact, at a phase transition point between two phases 1 and 2, there is a coexistence of phases 1 and 2. A division of the PT-plane (or any other choice of variables) into regions of mutually distinct phases and their coexistence regions is called the *phase diagram* of the system.

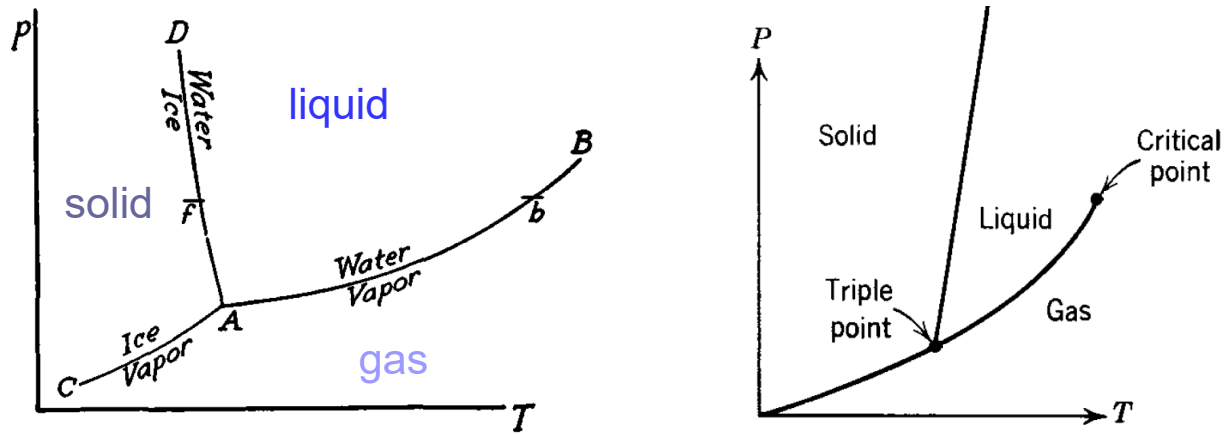


Figure 5.1: *Left.* Phase diagram of water: AB—coexistence curve of liquid and gas phases, AC—coexistence curve of solid and gas phase, AD—coexistence curve of solid and liquid phase, A—triple point, f—freezing point at $P = 1$ atm, b—boiling point at $P = 1$ atm. The slope of the melting curve AD represents the anomaly of water ($\frac{dP}{dT}|_{\text{melt}} < 0$). *Right.* Phase diagram of a generic substance (without anomaly in the melting curve).

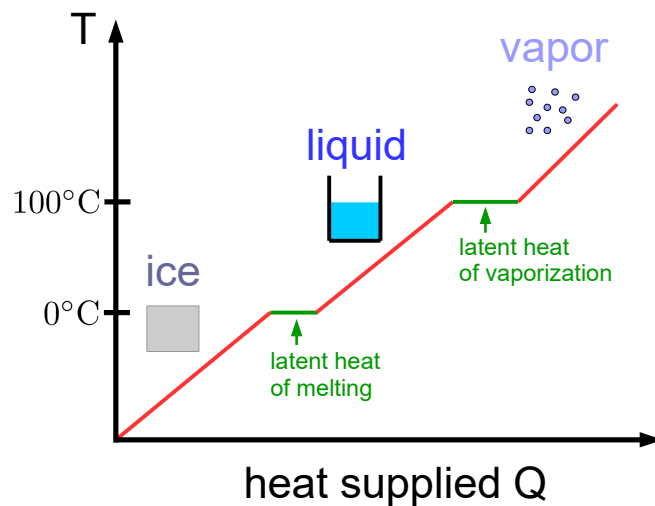
At the *triple point* of water located at

$$T_{\text{tr}} = 0.0075^\circ\text{C}, \quad (5.107)$$

$$P_{\text{tr}} = 0.00602 \text{ atm}, \quad (5.108)$$

the solid, liquid, and gas phases of water coexist in equilibrium. One can show that such a coexistence region is necessarily an isolated point in the PT -plane. This and similar geometric statements follow from the so-called Gibbs phase rule.

Latent heat. Consider a homogeneous system of water in its solid phase. We add heat Q to the system to increase its temperature at constant pressure $P = 1$ atm. The system undergoes a melting and vaporization transition at temperatures $T_f(P) = 0^\circ\text{C}$ and $T_v(P) = 100^\circ\text{C}$. The diagram of temperature vs. heat supplied, looks like this:

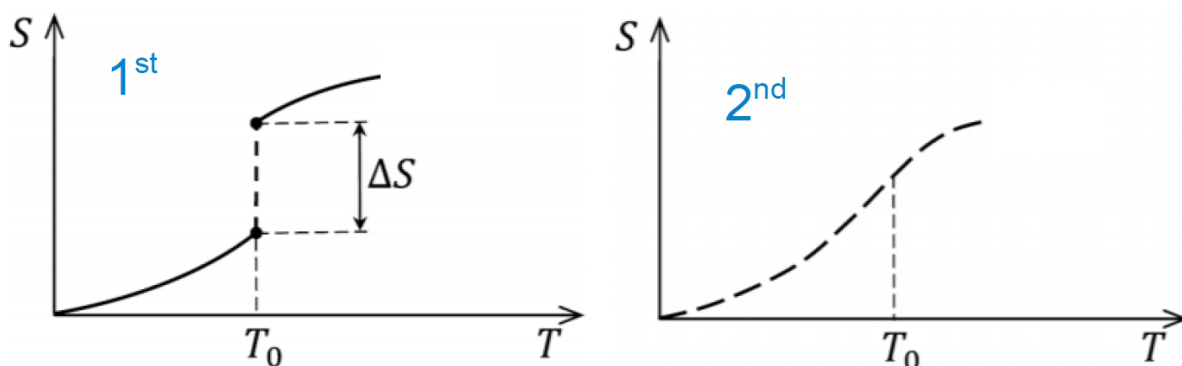


When the system turns from a solid to a liquid, the temperature remains constant and the heat supplied is used within the substance to break some chemical bonds and modify its internal structure. This costs energy that cannot be used to increase temperature. The amount of heat Q_{lat} which does not lead to a temperature increase is called *latent heat*. Similarly, when the system turns from a liquid to a gas, latent heat of vaporization needs to be supplied.

First and second order transitions. A phase transition with nonzero latent heat is called a *first-order phase transition*. Whereas the thermodynamic potentials such as $F(T, V, N)$ or $G(T, P, N)$ remain continuous at the transition or “critical” temperature T_0 , the entropy $S = -(\frac{\partial F}{\partial T})_{V, N} = -(\frac{\partial G}{\partial T})_{P, N}$ jumps by an amount

$$\Delta S = \frac{Q_{\text{lat}}}{T_0} \quad (5.109)$$

upon increasing temperature through the transition. A phase transition where the entropy remains continuous, and hence there is no latent heat, is called a *second-order phase transition*. Crucially, we see that derivatives of thermodynamic potentials are not always continuous at a phase transition—they may have kinks and jumps.



In water, all phase transitions are of first order, except for the so-called *critical point*, which is the end-point of the condensation curve AB located at

$$T_c = 374^\circ\text{C}, \quad (5.110)$$

$$P_c = 218 \text{ atm}. \quad (5.111)$$

For $P > P_c$, pressures are so high that liquid water and vapor are no longer distinct phases. Exactly at the critical point, water and vapor coexist and show the phenomenon of critical opalescence, which is an enhanced scattering of light that makes the substance appear milky. This is an example of a larger class of so-called *critical phenomena*, which universally appear at second-order phase transitions.

6 Kinetic theory of gases

6.1 Brief review of classical mechanics

This section is to review some notion of classical mechanics and fix our notation.

Notation. We consider systems of particles in three dimensions. Vector quantities, such as momentum and position, will be indicated by an arrow,

$$\vec{p} = \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix}, \quad \vec{x} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \quad (6.1)$$

The set of all values of \vec{p} and \vec{x} is called momentum and position space, respectively. The three components of a vector are labelled by indices $i, j, \dots \in \{1, 2, 3\}$, i.e. p_i and x_i . We denote

$$p := |\vec{p}| = \sqrt{p_x^2 + p_y^2 + p_z^2}, \quad (6.2)$$

$$r := |\vec{x}| = \sqrt{x^2 + y^2 + z^2}. \quad (6.3)$$

We define the scalar product

$$\vec{a} \cdot \vec{b} = a_1 b_1 + a_2 b_2 + a_3 b_3. \quad (6.4)$$

If $\vec{a} = \vec{b}$, we write

$$\vec{a}^2 = \vec{a} \cdot \vec{a}. \quad (6.5)$$

This implies that

$$p = \sqrt{\vec{p}^2}, \quad r = \sqrt{\vec{x}^2}. \quad (6.6)$$

A derivative with respect to p_i or x_i is denoted

$$\frac{\partial}{\partial p_i} = \partial_{p_i}, \quad \frac{\partial}{\partial x_i} = \partial_{x_i}. \quad (6.7)$$

The nabla operator is defined as

$$\nabla_{\vec{p}} = \begin{pmatrix} \partial_{p_1} \\ \partial_{p_2} \\ \partial_{p_3} \end{pmatrix}, \quad \nabla_{\vec{x}} = \begin{pmatrix} \partial_{x_1} \\ \partial_{x_2} \\ \partial_{x_3} \end{pmatrix} = \begin{pmatrix} \partial_x \\ \partial_y \\ \partial_z \end{pmatrix}. \quad (6.8)$$

It is also customary to write

$$\frac{\partial}{\partial \vec{p}} = \nabla_{\vec{p}}, \quad \frac{\partial}{\partial \vec{x}} = \nabla_{\vec{x}}. \quad (6.9)$$

These formulas are to be understood as acting on some function $f(\vec{x}, \vec{p})$, for instance

$$\nabla_{\vec{x}} f = \frac{\partial f}{\partial \vec{x}} = \begin{pmatrix} \frac{\partial f}{\partial x} \\ \frac{\partial f}{\partial y} \\ \frac{\partial f}{\partial z} \end{pmatrix}. \quad (6.10)$$

A volume integral in three spatial dimensions is

$$\int dx \int dy \int dz f(\vec{x}, \vec{p}) = \int d^3x f(\vec{x}, \vec{p}), \quad (6.11)$$

where we introduce the volume element

$$d^3x := dx dy dz. \quad (6.12)$$

Similarly,

$$d^3p = dp_1 dp_2 dp_3. \quad (6.13)$$

The integration boundaries for each of the integrals depend on the context and need to be specified. If we are integrating over a volume V in position space, we also write

$$\int_V d^3x f(\vec{x}, \vec{p}). \quad (6.14)$$

For instance, if $V = L^3$ is a cube of side lengths L , we have

$$\int_V d^3x f(\vec{x}, \vec{p}) = \int_{-L/2}^{L/2} dx \int_{-L/2}^{L/2} dy \int_{-L/2}^{L/2} dz f(\vec{x}, \vec{p}). \quad (6.15)$$

If no volume or boundaries are specified, it is usually assumed that we integrate over all possible values, i.e. \mathbb{R}^3 ,

$$\int d^3p f(\vec{x}, \vec{p}) = \int_{\mathbb{R}^3} d^3p f(\vec{x}, \vec{p}) = \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z f(\vec{x}, \vec{p}). \quad (6.16)$$

For such an integral to be finite or meaningful, the function $f(\vec{x}, \vec{p})$ needs to decay sufficiently fast as each of the components p_i approaches $\pm\infty$. The three most important coordinate systems are

$$\text{Cartesian: } \vec{x} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \quad \int d^3x f(\vec{x}) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz f(\vec{x}), \quad (6.17)$$

$$\text{cylindrical: } \vec{x} = \begin{pmatrix} r_{\perp} \cos \phi \\ r_{\perp} \sin \phi \\ z \end{pmatrix}, \quad \int d^3x f(\vec{x}) = \int_0^{\infty} dr_{\perp} \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} dz r_{\perp} f(\vec{x}), \quad (6.18)$$

$$\text{spherical: } \vec{x} = \begin{pmatrix} r \cos \phi \sin \theta \\ r \sin \phi \sin \theta \\ r \cos \theta \end{pmatrix}, \quad \int d^3x f(\vec{x}) = \int_0^{\infty} dr \int_0^{2\pi} d\phi \int_0^{\pi} d\theta r^2 \sin \theta f(\vec{x}). \quad (6.19)$$

Exercise: Compute the volumes of a cube, cylinder, and sphere using a suitable coordinate system.

Example for volume integral. Consider the so-called *Gaussian distribution function*

$$f(\vec{x}, \vec{p}) = e^{-A(\vec{p} - \vec{p}_0)^2}, \quad (6.20)$$

with $A > 0, \vec{p}_0$ some constants. We want to compute the integral

$$I = \int_V d^3x \int d^3p f(\vec{x}, \vec{p}). \quad (6.21)$$

Since $f(\vec{x}, \vec{p})$ does not depend on \vec{x} , we have

$$I = \underbrace{\left(\int_V d^3x 1 \right)}_V \int d^3p f(\vec{x}, \vec{p}) = V \int d^3p f(\vec{x}, \vec{p}). \quad (6.22)$$

Writing $\vec{p}_0 = (p_{0x}, p_{0y}, p_{0z})$ we have

$$f(\vec{x}, \vec{p}) = e^{-A[(p_x - p_{0x})^2 + (p_y - p_{0y})^2 + (p_z - p_{0z})^2]} = e^{-A(p_x - p_{0x})^2} e^{-A(p_y - p_{0y})^2} e^{-A(p_z - p_{0z})^2}, \quad (6.23)$$

and so

$$I = V \left(\int_{-\infty}^{\infty} dp_x e^{-A(p_x - p_{0x})^2} \right) \left(\int_{-\infty}^{\infty} dp_y e^{-A(p_y - p_{0y})^2} \right) \left(\int_{-\infty}^{\infty} dp_z e^{-A(p_z - p_{0z})^2} \right). \quad (6.24)$$

We introduce the shifted variables $p_i \rightarrow p'_i = p_i - p_{0i}$ and see that the integrals becomes independent of \vec{p}_0 ,

$$I = V \left(\int_{-\infty}^{\infty} dp'_x e^{-A(p'_x)^2} \right) \left(\int_{-\infty}^{\infty} dp'_y e^{-A(p'_y)^2} \right) \left(\int_{-\infty}^{\infty} dp'_z e^{-A(p'_z)^2} \right) \quad (6.25)$$

$$=: VJ^3. \quad (6.26)$$

Each of the three integrals has the same value J . It can be computed as follows:

$$J = \int_{-\infty}^{\infty} dx e^{-Ax^2} \quad (6.27)$$

$$J^2 = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy e^{-A(x^2 + y^2)} \quad (6.28)$$

$$= \int_0^{\infty} dr r \int_0^{2\pi} d\phi e^{-Ar^2}, \quad \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} r \cos \phi \\ r \sin \phi \end{pmatrix} \quad (6.29)$$

$$= 2\pi \int_0^{\infty} dr r e^{-Ar^2} \quad (6.30)$$

$$= 2\pi \left. \frac{e^{-Ar^2}}{-2A} \right|_{r=0}^{\infty} \quad (6.31)$$

$$= \frac{\pi}{A}, \quad (6.32)$$

so

$$J = \int_{-\infty}^{\infty} dx e^{-Ax^2} = \sqrt{\frac{\pi}{A}}. \quad (6.33)$$

Comment: J is called a *Gaussian integral*.

We eventually arrive at

$$I = V \left(\frac{\pi}{A} \right)^{3/2}. \quad (6.34)$$

N-particle systems. We consider a system of N particles in three dimensions. The particles are labelled by the indices $a, b, \dots \in \{1, \dots, N\}$. The vectors corresponding to each of the N particles are \vec{p}_a and \vec{x}_a . The i th component of the momentum of the a th particle is indicated by a double index, p_{ai} . A dynamical state of the system is specified by the positions and momenta of all particles. The total energy of a dynamical state is given by the Hamiltonian function

$$\mathcal{H} = \mathcal{H}(\vec{x}_1, \dots, \vec{x}_N, \vec{p}_1, \dots, \vec{p}_N). \quad (6.35)$$

This splits into kinetic and potential energy according to

$$\mathcal{H} = \mathcal{H}_{\text{kin}} + \mathcal{H}_{\text{pot}} \quad (6.36)$$

with

$$\mathcal{H}_{\text{kin}} = \sum_{a=1}^N \frac{\vec{p}_a^2}{2m}, \quad (6.37)$$

$$\mathcal{H}_{\text{pot}} = \sum_{a=1}^N \mathcal{V}_{\text{ex}}(\vec{x}_a) + \frac{1}{2} \sum_{a,b=1}^N \mathcal{V}_{\text{int}}(|\vec{x}_a - \vec{x}_b|). \quad (6.38)$$

Here $\mathcal{V}_{\text{ex}}(\vec{x})$ is an external potential and $\mathcal{V}_{\text{int}}(r)$ is the interaction energy between two particles at distance r . For instance, $\mathcal{V}_{\text{ex}}(\vec{x})$ could be Earth's gravitational field,

$$\mathcal{V}_{\text{ex}}(\vec{x}) = mgz, \quad (6.39)$$

and $\mathcal{V}_{\text{int}}(r)$ could be a molecular Lennard–Jones type, electrostatic Coulomb, or gravitational Newtonian potential,

$$\mathcal{V}_{\text{int}}(r) = \begin{cases} \frac{\sigma}{r^{12}} - \frac{\tau}{r^6} \\ \frac{1}{4\pi\epsilon} \frac{q_1 q_2}{r} \\ -G \frac{m_1 m_2}{r} \end{cases} \quad (6.40)$$

The force acting on particle a is

$$\vec{F}_a = -\frac{\partial \mathcal{H}_{\text{pot}}}{\partial \vec{x}_a} = -\nabla_{\vec{x}_a} \mathcal{H}_{\text{pot}}. \quad (6.41)$$

The velocity is

$$\vec{v}_a = \frac{\vec{p}_a}{m} = \dot{\vec{x}}_a, \quad (6.42)$$

and Newton's equation of motion reads

$$\ddot{\vec{x}}_a = \frac{\vec{F}_a}{m}. \quad (6.43)$$

A non-interacting (= ideal) system has $\mathcal{V}_{\text{int}}(r) = 0$, and so

$$\mathcal{H} = \sum_{a=1}^N \mathcal{H}_1(\vec{x}_a, \vec{p}_a) \quad (6.44)$$

with single-particle Hamiltonian

$$\mathcal{H}_1(\vec{x}, \vec{p}) = \frac{\vec{p}^2}{2m} + \mathcal{V}_{\text{ex}}(\vec{x}). \quad (6.45)$$

6.2 Boltzmann equation

Kinetic theory explains all macroscopic properties of gases through the motion of atoms and their collisions— with each other and with the walls of the container. Its success in explaining thermodynamic phenomena significantly contributed to the acceptance of the atomic hypothesis.

For a thermodynamic system with fixed parameters such as (T, V, N) , we do not attempt to trace the positions and momenta of all individual particles. Instead, we pick an arbitrary particle and denote by

$$f(\vec{x}, \vec{p}, t) \quad (6.46)$$

a distribution function that is proportional to the probability that this particle is at position \vec{x} with momentum \vec{p} at time t . Obviously, if we know $f(\vec{x}, \vec{p}, t)$, we know how the system behaves as a collection of particles. More precisely, we choose a normalization such that

$$dN = f(\vec{x}, \vec{p}, t) d^3x d^3p \quad (6.47)$$

is the number of particles located inside a small cube of volume d^3x around the position \vec{x} , and a small cube d^3p around \vec{p} in momentum space. One should think of d^3x and d^3p as containing a macroscopic number of particles. For instance, for a gas at room temperature we have $n \sim 10^{19} \text{cm}^{-3}$, so a volume of $d^3x = (1 \mu\text{m})^3 = 10^{-18} \text{m}^3 = 10^{-12} \text{cm}^3$ would appear pointlike to us, although it still contains 10^7 particles. The total number of particles is

$$N = \int dN = \int_V d^3x \int d^3p f(\vec{x}, \vec{p}, t) \quad (6.48)$$

at any time t . The local number density of particles at position \vec{x} (with any momentum \vec{p}) is

$$n(\vec{x}) = \int d^3p f(\vec{x}, \vec{p}, t), \quad (6.49)$$

and

$$N = \int_V d^3x n(\vec{x}). \quad (6.50)$$

The *momentum distribution* of particles with momentum \vec{p} (at any position \vec{x}) is

$$\tilde{n}(\vec{p}) = \int_V d^3x f(\vec{x}, \vec{p}, t), \quad (6.51)$$

with

$$N = \int d^3p \tilde{n}(\vec{p}). \quad (6.52)$$

Boltzmann equation. The Boltzmann equation is the equation of motion for $f(\vec{x}, \vec{p}, t)$ in time. For this, consider a particle with (\vec{x}, \vec{p}) at time t . At a later time $t' = t + \delta t$, with δt infinitesimal, it will have coordinates

$$\vec{x}' = \vec{x} + \vec{v}\delta t = \vec{x} + \frac{\vec{p}}{m}\delta t, \quad (6.53)$$

$$\vec{p}' = \vec{p} + \vec{F}\delta t, \quad (6.54)$$

where \vec{v} is the velocity of the particle and $\vec{F} = -\nabla_{\vec{x}}\mathcal{V}_{\text{ex}}$ the external force acting on the particle.⁵ If there are no collisions (interactions) among the particles, we have

$$f(\vec{x}, \vec{p}, t) = f(\vec{x}', \vec{p}', t'), \quad (6.55)$$

because the probability to find the particle "moves" along with the particle's trajectory, or

$$f\left(\vec{x} + \frac{\vec{p}}{m}\delta t, \vec{p} + \vec{F}\delta t, t + \delta t\right) - f(\vec{x}, \vec{p}, t) = 0. \quad (6.56)$$

In the limit $\delta t \rightarrow 0$ we obtain

⁵In the presence of interactions, $\mathcal{V}_{\text{int}} \neq 0$, there is a mean-field contribution to \vec{F} that we will ignore in the following.

$$\left(\partial_t + \frac{\vec{p}}{m} \cdot \nabla_{\vec{x}} + \vec{F} \cdot \nabla_{\vec{p}}\right) f(\vec{x}, \vec{p}, t) = 0. \quad (6.57)$$

$$\text{Boltzmann equation for non-interacting particles} \quad (6.58)$$

Example. Consider non-interacting particles without external forces. The solution to the Boltzmann equation

$$\left(\partial_t + \vec{v} \cdot \nabla_{\vec{x}}\right) f(\vec{x}, \vec{p}, t) = 0 \quad (6.59)$$

is any function of the form

$$f(\vec{x}, \vec{p}, t) = \varphi(\vec{x} - \vec{v}t). \quad (6.60)$$

This is a traveling wave. Since the initial distribution is

$$f(\vec{x}, \vec{p}, 0) = \varphi(\vec{x}), \quad (6.61)$$

we have

$$f(\vec{x}, \vec{p}, t) = f(\vec{x} - \vec{v}t, \vec{p}, 0). \quad (6.62)$$

Collision integral. In the presence of interactions,

$$f(\vec{x}, \vec{p}, t) \neq f(\vec{x}', \vec{p}', t'), \quad (6.63)$$

because a particle that started at (\vec{x}, \vec{p}) at t might be scattered away and not end up at (\vec{x}', \vec{p}') at t' , or scattered particles that did not start at (\vec{x}, \vec{p}) at t might appear at (\vec{x}', \vec{p}') at t' . We define the *collision integral* as the difference,

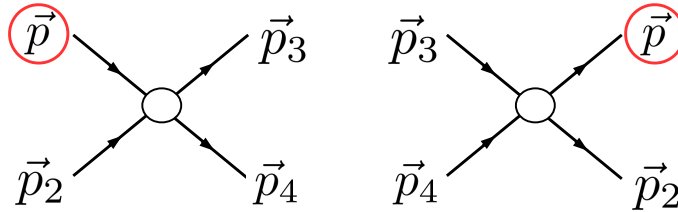
$$f(\vec{x} + \vec{v}\delta t, \vec{p} + \vec{F}\delta t, t + \delta t) - f(\vec{x}, \vec{p}, t) =: \mathcal{I}_{\text{coll}}\delta t, \quad (6.64)$$

hence

$$\left(\partial_t + \frac{\vec{p}}{m} \cdot \nabla_{\vec{x}} + \vec{F} \cdot \nabla_{\vec{p}}\right) f(\vec{x}, \vec{p}, t) = \mathcal{I}_{\text{coll}}. \quad (6.65)$$

$$\text{Boltzmann equation} \quad (6.66)$$

For simplicity assume that $f(\vec{x}, \vec{p}, t)$ does not depend on \vec{x} . Consider then a collision where our particle with momentum \vec{p} scatters elastically with a particle of momentum \vec{p}_2 into two particles with final momentum \vec{p}_3 and \vec{p}_4 . Similarly, consider two particles with initial momenta \vec{p}_3 and \vec{p}_4 that scatter elastically into particles with momenta \vec{p} and \vec{p}_2 :



The number of events of the first kind (which decrease f) is proportional to $f(\vec{p}, t)f(\vec{p}_2, t)$, which is the probability to find this initial configuration.⁶ Similarly, the number of events of the second kind (which

⁶We assume *molecular chaos* here, where the momenta of the two particles are uncorrelated and the probability factorizes.

increase f) is proportional to $f(\vec{p}_3, t)f(\vec{p}_4, t)$. We have

$$\mathcal{I}_{\text{coll}} = \int d^3 p_2 \int d^3 p_3 \int d^3 p_4 \mathcal{M}(\vec{p}, \vec{p}_2; \vec{p}_3, \vec{p}_4) \left[-f(\vec{p}, t)f(\vec{p}_2, t) + f(\vec{p}_3, t)f(\vec{p}_4, t) \right]. \quad (6.67)$$

In an elastic collision, energy and momentum are conserved, thus the momenta are constrained by

$$(*) \begin{cases} \vec{p} + \vec{p}_2 = \vec{p}_3 + \vec{p}_4, \\ \frac{\vec{p}^2}{2m} + \frac{\vec{p}_2^2}{2m} = \frac{\vec{p}_3^2}{2m} + \frac{\vec{p}_4^2}{2m} \end{cases}. \quad (6.68)$$

The function \mathcal{M} encodes the details of the interaction, and is not important for us here. A typical form is

$$\mathcal{M}(\vec{p}, \vec{p}_2; \vec{p}_3, \vec{p}_4) = \tilde{\mathcal{V}}_{\text{int}}(\vec{q}) \delta\left(\frac{\vec{p}^2}{2m} + \frac{\vec{p}_2^2}{2m} - \frac{\vec{p}_3^2}{2m} - \frac{\vec{p}_4^2}{2m}\right) \delta^{(3)}(\vec{p} + \vec{p}_2 - \vec{p}_3 - \vec{p}_4), \quad (6.69)$$

with momentum transfer $\vec{q} = \vec{p}_3 - \vec{p}$ and $\tilde{\mathcal{V}}_{\text{int}}(\vec{q})$ the Fourier transform of the interaction potential $\mathcal{V}_{\text{int}}(r)$.

6.3 Maxwell–Boltzmann distribution

Our goal is to determine the *equilibrium distribution function* $f_0(\vec{x}, \vec{p})$ defined as the solution of the Boltzmann equation that is independent of time. For large times, any solution $f(\vec{x}, \vec{p}, t)$ will behave as

$$f(\vec{x}, \vec{p}, t) \xrightarrow{t \rightarrow \infty} f_0(\vec{x}, \vec{p}), \quad (6.70)$$

which we associate with the equilibration process. For a homogeneous system, i.e. in the absence of external potentials, $\mathcal{V}_{\text{ex}}(\vec{x}) = 0$, the system is translation invariant and so f_0 cannot depend on \vec{x} . Consequently,

$$f_0(\vec{x}, \vec{p}) = f_0(\vec{p}) = \frac{\tilde{n}_0(p)}{V}. \quad (6.71)$$

Furthermore, $\vec{F} = -\nabla_{\vec{x}} \mathcal{V}_{\text{ex}} = 0$ and so the Boltzmann equation reads

$$\partial_t f_0(\vec{p}, t) = \mathcal{I}_{\text{coll}}. \quad (6.72)$$

The equilibrium distribution satisfying $\partial_t f_0 = 0$ is then determined from

$$\mathcal{I}_{\text{coll}} = 0. \quad (6.73)$$

A sufficient (and, one can show, necessary) condition for this to hold is

$$f_0(\vec{p})f_0(\vec{p}_2) = f_0(\vec{p}_3)f_0(\vec{p}_4), \quad (6.74)$$

or, taking the logarithm

$$\ln f_0(\vec{p}) + \ln f_0(\vec{p}_2) = \ln f_0(\vec{p}_3) + \ln f_0(\vec{p}_4). \quad (6.75)$$

This has the form of a conservation law, since (\vec{p}, \vec{p}_2) and (\vec{p}_3, \vec{p}_4) can be *any* momenta that satisfy momentum and energy conservation. If $\chi(\vec{p})$ is any quantity associated to a particle with momentum \vec{p} , so that $\chi(\vec{p}_1) + \chi(\vec{p}_2)$ is conserved in an elastic collision between two particles with \vec{p}_1 and \vec{p}_2 , then the most general solution is

$$\ln f_0(\vec{p}) = \chi_1(\vec{p}) + \chi_2(\vec{p}) + \dots, \quad (6.76)$$

where $\chi_1(\vec{p}), \chi_2(\vec{p}), \dots$ is a list of all independently conserved quantities. For point-particles, these are the energy and momentum of the particle, see Eqs. (*), and, of course, a constant. Hence the most general form is

$$\ln f_0(\vec{p}) = A' \frac{\vec{p}^2}{2m} + \vec{B}' \cdot \vec{p} + C' \quad (6.77)$$

$$= -A(\vec{p} - \vec{p}_0)^2 + C \quad (6.78)$$

with suitable constants $A' = -2mA$, $\vec{B}' = 2A\vec{p}_0$, $C' = C - A\vec{p}_0^2$. We conclude that the stable equilibrium distribution is given by

$$f_0(\vec{p}) = \frac{\tilde{n}_0(\vec{p})}{V} = \frac{1}{\mathcal{N}} e^{-A(\vec{p}-\vec{p}_0)^2} \quad (6.79)$$

where \mathcal{N} is a normalization constant. We define the expectation value of a function $g = g(\vec{x}, \vec{p})$ in equilibrium as

$$\langle g \rangle = \int_V d^3x \int d^3p g(\vec{x}, \vec{p}) f_0(\vec{p}). \quad (6.80)$$

Note that $\langle g \rangle$ is extensive because of the volume integral $\int_V d^3x$.

Fixing the constants. We first normalize f_0 such that

$$N \stackrel{!}{=} \int_V d^3x \int d^3p f_0(\vec{p}) = \frac{V}{\mathcal{N}} \int d^3p e^{-A(\vec{p}-\vec{p}_0)^2} = \frac{V}{\mathcal{N}} \left(\frac{\pi}{A}\right)^{3/2}, \quad (6.81)$$

thus

$$\mathcal{N} = \frac{V}{N} \left(\frac{\pi}{A}\right)^{3/2}. \quad (6.82)$$

The average momentum of a gas particle is

$$\langle \vec{p} \rangle = \frac{\langle \vec{p}_{\text{tot}} \rangle}{N} = \frac{1}{N} \int_V d^3x \int d^3p \vec{p} f_0(\vec{p}) \quad (6.83)$$

$$= \frac{1}{N} \frac{1}{\mathcal{N}} \int_V d^3x \int d^3p \vec{p} e^{-A(\vec{p}-\vec{p}_0)^2} \quad (6.84)$$

$$= \frac{1}{N} \left(\frac{1}{\mathcal{N}} \int_V d^3x \int d^3p \vec{p}_0 e^{-A(\vec{p}-\vec{p}_0)^2} + \underbrace{\frac{1}{\mathcal{N}} \int_V d^3x \int d^3p (\vec{p} - \vec{p}_0) e^{-A(\vec{p}-\vec{p}_0)^2}}_0 \right) \quad (6.85)$$

$$= \frac{\vec{p}_0}{N} \underbrace{\int_V d^3x \int d^3p f_0(\vec{p})}_N \quad (6.86)$$

$$= \vec{p}_0. \quad (6.87)$$

We used that for an even function $\eta(\vec{x}) = \eta(-\vec{x})$ we have

$$\int d^3x \vec{x} \eta(\vec{x}) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \begin{pmatrix} x \\ y \\ z \end{pmatrix} \eta(\vec{x}) = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \quad (6.88)$$

So \vec{p}_0 is the average momentum of particles. For a system that does not move as a whole, we must therefore choose

$$\vec{p}_0 = 0. \quad (6.89)$$

Indeed, for all particles with \vec{p} , there should be an equal number of particles with $-\vec{p}$. At last we determine A . We write

$$A = \frac{\beta}{2m} \quad (6.90)$$

and

$$f_0(\vec{p}) = n \left(\frac{\beta}{2\pi m} \right)^{3/2} e^{-\beta p^2/(2m)}. \quad (6.91)$$

We determine β from the pressure. Consider a container wall in the yz -plane and gas particles impinging on it from the left with positive $p_x > 0$. The number of particles hitting an area \mathcal{A} of the wall in a time-interval Δt , i.e. the number of collisions, is given by

$$dN_{\text{coll}} = \frac{1}{2} f_0(\vec{p}) \underbrace{\mathcal{A} \Delta x}_{\Delta V} d^3 p = \frac{1}{2} f_0(\vec{p}) \mathcal{A} v_x \Delta t d^3 p = \frac{1}{2m} f_0(\vec{p}) \mathcal{A} p_x \Delta t d^3 p. \quad (6.92)$$

The factor $\frac{1}{2}$ accounts for the fact that we only consider half the particles due to $p_x > 0$. The momentum transfer onto the wall per collision is

$$\Delta p_x = 2p_x, \quad (6.93)$$

so the force onto the wall per collision is

$$F_x = \frac{\Delta p_x}{\Delta t} = \frac{2p_x}{\Delta t}. \quad (6.94)$$

Hence

$$P = \frac{\langle F_x \rangle}{\mathcal{A}} = \frac{1}{\mathcal{A}} \int dN_{\text{coll}} \frac{2p_x}{\Delta t} \quad (6.95)$$

$$= \frac{1}{m} \int d^3 p p_x^2 f_0(\vec{p}) \quad (6.96)$$

$$= \frac{1}{m} \frac{1}{\mathcal{N}} \underbrace{\left(\int_{-\infty}^{\infty} dp_x p_x^2 e^{-Ap_x^2} \right)}_{\frac{1}{2A} \sqrt{\frac{\pi}{A}}} \underbrace{\left(\int_{-\infty}^{\infty} dp_y e^{-Ap_y^2} \right)}_{\sqrt{\frac{\pi}{A}}} \underbrace{\left(\int_{-\infty}^{\infty} dp_z e^{-Ap_z^2} \right)}_{\sqrt{\frac{\pi}{A}}} \quad (6.97)$$

$$= \frac{1}{m} n \left(\frac{A}{\pi} \right)^{3/2} \times \frac{1}{2A} \left(\frac{\pi}{A} \right)^{3/2} \quad (6.98)$$

$$= \frac{n}{2mA} = \frac{n}{\beta}. \quad (6.99)$$

We used that

$$\int_{-\infty}^{\infty} dx x^2 e^{-Ax^2} = -\frac{\partial}{\partial A} \int_{-\infty}^{\infty} dx e^{-Ax^2} = -\frac{\partial}{\partial A} \sqrt{\frac{\pi}{A}} = \frac{\pi^{1/2}}{2A^{3/2}}, \quad (6.100)$$

which is another Gaussian integral. Since the absolute temperature is defined such that

$$P = nk_B T \quad (6.101)$$

for an ideal gas, which also holds for very weakly interacting gases, we conclude that

$$\beta = \frac{1}{k_B T}. \quad (6.102)$$

The equilibrium distribution becomes

$$f_0(\vec{p}) = \frac{n}{(2\pi m k_B T)^{3/2}} e^{-p^2/(2m k_B T)} \quad (6.103)$$

$$\text{Maxwell-Boltzmann distribution.} \quad (6.104)$$

Note that the rotation-invariant or isotropic form of $f_0(\vec{p})$, which only depends on the magnitude $p = |\vec{p}|$, implies that

$$\langle p_x^2 \rangle = \langle p_y^2 \rangle = \langle p_z^2 \rangle. \quad (6.105)$$

Furthermore,

$$\langle p^2 \rangle = \int_V d^3x \int d^3p (p_x^2 + p_y^2 + p_z^2) f_0(\vec{p}) = 3\langle p_x^2 \rangle. \quad (6.106)$$

The average energy per particle is

$$\frac{\langle E \rangle}{N} = \frac{1}{N} \int_V d^3x \int d^3p \frac{p^2}{2m} f_0(\vec{p}) \quad (6.107)$$

$$= \frac{1}{2mN} \langle p^2 \rangle \quad (6.108)$$

$$= \frac{3}{2mN} \langle p_x^2 \rangle \quad (6.109)$$

$$= \frac{3}{2mN} V \times mP \quad (6.110)$$

$$= \frac{3PV}{2N} = \frac{3}{2} k_B T. \quad (6.111)$$

Hence we obtained from kinetic theory that

$$E = \frac{3}{2} PV, \quad (6.112)$$

$$E = \frac{3}{2} N k_B T \quad (6.113)$$

for point-like particles, i.e. monoatomic gases. The equilibrium distribution $h_0(p)$ of magnitudes p (instead of \vec{p}), defined from

$$\int d^3p f_0(\vec{p}) = 4\pi \int_0^\infty dp p^2 f_0(\vec{p}) =: \int_0^\infty dp h_0(p), \quad (6.114)$$

is given by

$$h_0(p) = 4\pi p^2 f_0(\vec{p}) = n \left(\frac{8}{\pi^3 m k_B T} \right)^{3/2} p^2 e^{-p^2/(2mk_B T)}. \quad (6.115)$$

For small momenta we have

$$h_0(p) \sim p^2, \quad (6.116)$$

for large momenta we have

$$h_0(p) \sim p^2 e^{-\beta p^2/(2m)}. \quad (6.117)$$

Exercise: Show that the most probable momentum, \bar{p} , defined as the momentum such that

$$h_0(p) = 4\pi p^2 f_0(\vec{p}) \quad (6.118)$$

is maximal, is given by

$$\bar{p} = \sqrt{2mk_B T}, \quad (6.119)$$

whereas the root mean square momentum, defined through

$$p_{\text{rms}}^2 = \frac{\langle p^2 \rangle}{N} = \frac{1}{N} \int_V d^3x \int d^3p p^2 f_0(\vec{p}), \quad (6.120)$$

is given by

$$p_{\text{rms}} = \sqrt{3mk_{\text{B}}T}. \quad (6.121)$$

Example. For a gas of molecular nitrogen N_2 ($m = 2 \times 14$ u) at room temperature ($T = 293$ K), we have

$$\bar{v} = \sqrt{\frac{2k_{\text{B}}T}{m}} = 417 \frac{\text{m}}{\text{s}}, \quad (6.122)$$

$$v_{\text{rms}} = \sqrt{\frac{3k_{\text{B}}T}{m}} = 511 \frac{\text{m}}{\text{s}}. \quad (6.123)$$

6.4 Equipartition and virial theorem

For an ideal monoatomic gas of pointlike particles with Hamiltonian

$$\mathcal{H} = \sum_{a=1}^N \frac{p_a^2}{2m} = \sum_{a=1}^N \frac{1}{2m} (p_{ax}^2 + p_{ay}^2 + p_{az}^2), \quad (6.124)$$

the three momentum components $\vec{p} = (p_x, p_y, p_z)$ are the only degrees of freedom of a particle. We define

$$\langle \dots \rangle_1 = \frac{\langle \dots \rangle}{N} \quad (6.125)$$

as the average per particle. We have

$$\langle p_x^2 \rangle_1 = \frac{\langle p^2 \rangle_1}{3} = mk_{\text{B}}T \quad (6.126)$$

$$\Rightarrow \left\langle \frac{p_x^2}{2m} \right\rangle_1 = \frac{1}{2} k_{\text{B}}T \quad (6.127)$$

per particle, which yields

$$\langle E \rangle = \sum_{a=1}^N \left\langle \frac{p_a^2}{2m} \right\rangle_1 = 3 \sum_{a=1}^N \left\langle \frac{p_x^2}{2m} \right\rangle_1 = 3N \times \frac{1}{2} k_{\text{B}}T. \quad (6.128)$$

If the gas consists of *diatomic* molecules, each particle has five degrees of freedom. Indeed, besides the momentum \vec{p} there are two rotational degrees of freedom, associated to rotations about the x - and y -axis, where we assumed that the bond connecting both atoms is along the z -axis. This means that a rotation about the z -axis leaves the molecule invariant and would therefore not amount to an actual physical motion of the molecule. (Similarly, a pointlike particle has zero rotational degrees of freedom.) If I is the moment of inertia of the molecule and ω_i the angular velocity for rotation about the i -axis, then

$$\mathcal{H} = \sum_{a=1}^N \left[\frac{1}{2m} (p_{ax}^2 + p_{ay}^2 + p_{az}^2) + \frac{I}{2} (\omega_x^2 + \omega_y^2) \right]. \quad (6.129)$$

For such a diatomic gas we have

$$\langle E \rangle = 5N \times \frac{1}{2} k_B T \quad (6.130)$$

in equilibrium. More generally, for a gas of molecules with g degrees of freedom per molecule, we have

$$\langle E \rangle = g \times N \times \frac{1}{2} k_B T \quad (6.131)$$

$$\textit{equipartition theorem} \quad (6.132)$$

in equilibrium. This implies, of course that

$$\frac{C_V}{N} = \frac{g}{2} k_B. \quad (6.133)$$

The equipartition theorem is only valid at high temperatures, where quantum statistics can be neglected.

To prove the equipartition theorem, we write

$$\mathcal{H} = \sum_{a=1}^N \mathcal{H}_1(\vec{x}_a, \vec{p}_a) + \text{interactions}, \quad (6.134)$$

where $\mathcal{H}_1(\vec{x}, \vec{p})$ is the single-particle Hamiltonian and the interactions are assumed to be present, but weak. An analysis of the Boltzmann equation and the vanishing of the collision integral then shows that $\ln f_0$ is a sum of all conserved quantities. For a system at rest this yields

$$\ln f_0(\vec{x}, \vec{p}) = \beta \mathcal{H}_1(\vec{x}, \vec{p}) + C, \quad (6.135)$$

because energy is the only conserved quantity that is nonzero. Hence

$$f_0(\vec{x}, \vec{p}) = \frac{1}{\mathcal{N}} e^{-\beta \mathcal{H}_1(\vec{x}, \vec{p})}, \quad (6.136)$$

where \mathcal{N} is some normalization constant. For any function $A(\vec{x}, \vec{p})$, we have

$$0 = \int_V d^3x \int d^3p \frac{\partial}{\partial p_i} \left(A(\vec{x}, \vec{p}) f_0(\vec{x}, \vec{p}) \right) \quad (6.137)$$

$$= \int_V d^3x \int d^3p \left(\frac{\partial A}{\partial p_i} f_0 + A \frac{\partial f_0}{\partial p_i} \right) \quad (6.138)$$

$$= \int_V d^3x \int d^3p \left(\frac{\partial A}{\partial p_i} - \beta A \frac{\partial \mathcal{H}_1}{\partial p_i} \right) f_0 \quad (6.139)$$

$$= \left\langle \frac{\partial A}{\partial p_i} \right\rangle - \beta \left\langle A \frac{\partial \mathcal{H}_1}{\partial p_i} \right\rangle. \quad (6.140)$$

The integral vanishes if $A f_0$ decays sufficiently fast for large momenta. Hence

$$\left\langle A \frac{\partial \mathcal{H}_1}{\partial p_i} \right\rangle = k_B T \left\langle \frac{\partial A}{\partial p_i} \right\rangle, \quad (6.141)$$

and, similarly,

$$\left\langle A \frac{\partial \mathcal{H}_1}{\partial x_i} \right\rangle = k_B T \left\langle \frac{\partial A}{\partial x_i} \right\rangle. \quad (6.142)$$

Inserting, for instance, $A(\vec{x}, \vec{p}) = p_i$ or $A(\vec{x}, \vec{p}) = x_i$ this yields

$$\left\langle p_i \frac{\partial \mathcal{H}_1}{\partial p_i} \right\rangle_1 = k_B T, \quad (6.143)$$

$$\left\langle x_i \frac{\partial \mathcal{H}_1}{\partial x_i} \right\rangle_1 = k_B T. \quad (6.144)$$

More generally, if the full \mathcal{H} depends on any coordinate Z (position, momentum, angular velocity, ...), then

$$\left\langle Z \frac{\partial \mathcal{H}}{\partial Z} \right\rangle_1 = k_B T. \quad (6.145)$$

So if the Hamiltonian contains a term

$$\mathcal{H} = \frac{A}{2} Z^2 + \dots, \quad (6.146)$$

then $\frac{\partial \mathcal{H}_1}{\partial Z} = AZ$ and

$$\left\langle \frac{A}{2} Z^2 \right\rangle_1 = \frac{1}{2} \left\langle Z \frac{\partial \mathcal{H}}{\partial Z} \right\rangle_1 = \frac{1}{2} k_B T. \quad (6.147)$$

We associate each such quadratic term with a degree of freedom. This completes the proof.

Example. Dulong–Petit law. Consider a solid as a three-dimensional crystal lattice of atoms or ions. The positions of the N ions are labelled by x_{ai} , their momenta by p_{ai} . The Hamiltonian reads

$$\mathcal{H} = \sum_{a=1}^N \frac{\vec{p}_a^2}{2m} + \mathcal{H}_{\text{pot}}(\vec{x}_1, \dots, \vec{x}_N). \quad (6.148)$$

In the harmonic approximation, we assume that the positions \vec{x}_a only slightly deviate from their equilibrium positions $\vec{x}_{0,a}$ defined as the minima of \mathcal{H}_{pot} . The Hamiltonian can then be approximated by

$$\mathcal{H} = \sum_{a=1}^N \left(\frac{\vec{p}_a^2}{2m} + \frac{k}{2} \vec{u}_a^2 \right), \quad (6.149)$$

where $\vec{u}_a = \vec{x}_a - \vec{x}_{0,a}$ is the *displacement* of the a th ion. This is a three-dimensional harmonic oscillator with $g = 6$ degrees of freedom per ion. We conclude that

$$C_V = 3Nk_B \quad (6.150)$$

$$\text{Dulong–Petit law}, \quad (6.151)$$

which is a good approximation for $C_V \approx C_P$ of many solids at high temperatures.

Virial theorem. Consider a general Hamiltonian of the form

$$\mathcal{H} = \mathcal{H}_{\text{kin}}(\vec{p}_1, \dots, \vec{p}_N) + \mathcal{H}_{\text{pot}}(\vec{x}_1, \dots, \vec{x}_N). \quad (6.152)$$

For

$$\mathcal{H}_{\text{kin}} = \sum_{a=1}^N \frac{\vec{p}_a^2}{2m} \quad (6.153)$$

we have

$$\vec{p}_a \cdot \frac{\partial \mathcal{H}_{\text{kin}}}{\partial \vec{p}_a} = \vec{p}_a \cdot \frac{\partial}{\partial \vec{p}_a} \sum_{b=1}^N \frac{\vec{p}_b^2}{2m} \quad (6.154)$$

$$= \vec{p}_a \cdot \sum_{b=1}^N \frac{\vec{p}_b}{m} \delta_{ab} = \frac{\vec{p}_a^2}{m}. \quad (6.155)$$

Consequently,

$$\sum_{a=1}^N \left\langle \vec{p}_a \cdot \frac{\partial \mathcal{H}_{\text{kin}}}{\partial \vec{p}_a} \right\rangle = \sum_{a=1}^N \left\langle \frac{\vec{p}_a^2}{m} \right\rangle = 2 \langle \mathcal{H}_{\text{kin}} \rangle. \quad (6.156)$$

Since

$$\left\langle \vec{p}_a \cdot \frac{\partial \mathcal{H}_{\text{kin}}}{\partial \vec{p}_a} \right\rangle = \left\langle \vec{x}_a \cdot \frac{\partial \mathcal{H}_{\text{pot}}}{\partial \vec{x}_a} \right\rangle \quad (6.157)$$

we conclude that

$$2 \langle \mathcal{H}_{\text{kin}} \rangle = \sum_{a=1}^N \left\langle \vec{x}_a \cdot \frac{\partial \mathcal{H}_{\text{pot}}}{\partial \vec{x}_a} \right\rangle \quad (6.158)$$

$$\text{Virial theorem.} \quad (6.159)$$

More generally, one can show that if

$$\mathcal{H}_{\text{pot}}(\vec{x}_1, \dots, \vec{x}_N) \quad (6.160)$$

is a homogeneous function of degree n , i.e.

$$\mathcal{H}_{\text{pot}}(\lambda \vec{x}_1, \dots, \lambda \vec{x}_N) = \lambda^n \mathcal{H}_{\text{pot}}(\vec{x}_1, \dots, \vec{x}_N), \quad (6.161)$$

then

$$\sum_{a=1}^N \vec{x}_a \cdot \frac{\partial \mathcal{H}_{\text{pot}}}{\partial \vec{x}_a} = n \mathcal{H}_{\text{pot}}. \quad (6.162)$$

The kinetic energy is always homogeneous of degree two. For a potential of the form

$$\mathcal{H}_{\text{pot}}(\vec{x}_1, \dots, \vec{x}_N) = \sum_{a=1}^N c_a |\vec{x}_a|^n \quad (6.163)$$

we then obtain

$$2 \langle \mathcal{H}_{\text{kin}} \rangle = n \langle \mathcal{H}_{\text{pot}} \rangle. \quad (6.164)$$

This formula finds applications, for instance, in solids (harmonic potential, $n = 2$) and astrophysics (gravitational potential, $n = -1$).