Fundamentals of Thermodynamics and Applications
Ingo Müller · Wolfgang H. Müller

Fundamentals of Thermodynamics and Applications

With Historical Annotations and Many Citations from Avogadro to Zermelo

Springer
Preface

Thermodynamics is the much abused slave of many masters • physicists who love the totally impractical Carnot process, • mechanical engineers who design power stations and refrigerators, • chemists who are successfully synthesizing ammonia and are puzzled by photosynthesis, • meteorologists who calculate cloud bases and predict föhn, boraccia and scirocco, • physico-chemists who vulcanize rubber and build fuel cells, • chemical engineers who rectify natural gas and distil fermented potato juice, • metallurgists who improve steels and harden surfaces, • nutrition counselors who recommend a proper intake of calories, • mechanics who adjust heat exchangers, • architects who construe – and often misconstrue – chimneys, • biologists who marvel at the height of trees, • air conditioning engineers who design saunas and the ventilation of air plane cabins, • rocket engineers who create supersonic flows, et cetera.

Not all of these professional groups need the full depth and breadth of thermodynamics. For some it is enough to consider a well-stirred tank, for others a stationary nozzle flow is essential, and yet others are well-served with the partial differential equation of heat conduction.

It is therefore natural that thermodynamics is prone to mutilation; different group-specific meta-thermodynamics’ have emerged which serve the interest of the groups under most circumstances and leave out aspects that are not often needed in their fields. To stay with the metaphor of the abused slave we might say that in some fields his legs and an arm are cut off, because only one arm is needed; in other circumstances the brain of the slave has atrophied, because only his arms and legs are needed. Students love this reduction, because it enables them to avoid “nonessential” aspects of thermodynamics. But the practice is dangerous; it may backfire when a brain is needed.

In this book we attempt to exhibit the complete fundament of classical thermodynamics which consists of the equations of balance of mass, momentum and energy, and of constitutive equations which characterize the behavior of material bodies, mostly gases, vapors and liquids because, indeed, classical thermodynamics is often negligent of solids, – and so are we, although not entirely.

Many applications are treated in the book by specializing the basic equations; a brief look at the table of contents bears witness to that feature.

Modern thermodynamics is a lively field of research at extremely low and extremely high temperatures and for strongly rarefied gases and in nano-tubes, or nano-layers, where quantum effects occur. But such subjects are not treated in this book. Indeed, there is nothing here which is not at least 70 years old. We claim, however, that our presentation is systematic and we believe that classical thermodynamics should be taught as we present it. If it were, thermodynamics might shed the nimbus of a difficult subject which surrounds it among students.

Even classical thermodynamics is such a wide field that it cannot be fully described in all its ramifications in a relatively short book like this one. We had to
resign ourselves to that fact. And we have decided to omit all discussion of • empirical state functions, • temperature dependent specific heats of liquids and ideal gases, and • irreversible secondary effects in engines. Such phenomena affect the neat analytical structure of thermodynamic problems, and we have excluded them, although we know full well that they are close to the hearts and minds of engineers who may even, in fact, consider incalculable irreversibilities of technical processes as the essence of thermodynamics. We do not share that opinion.

In the second half of the 19th century and early in the 20th century thermodynamics was at the forefront of physics, and eminent physicists and chemists like Planck, Einstein and Haber were steeped in thermodynamics; actually the formula \( E = m c^2 \), which identifies energy as it were, is basically a contribution to thermodynamics. We have made an attempt to enliven the text by a great many mini-biographies and historical annotations which are somewhat relevant to the development of thermodynamics or, in other cases, they illustrate early misconceptions which may serve to highlight the difficult emergence of the basic concepts of the field. A prologue has been placed in front of the main chapters in order to avoid going into subjects which are by now so commonplace that they are taught in high schools.

Colleagues, co-workers, and students have contributed to this work, some significantly, others little, but all of them something:

Mark Warmbrunn has drawn the cartoons. Rudolf Hentschel and Marlies Hentschel have helped with the figures and part of the text.

Several teaching assistants have edited the text and converted it into Springer style: Matti Blume, Anja Klinnert, Volker Marhold, Christoph Menzel, Felix J. Müller.

Guido Harneit has given support with the computer.

Everyone of them deserves our sincere gratitude.

Berlin, in the summer of 2008

Ingo Müller & Wolfgang H. Müller
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P  Prologue on ideal gases and incompressible fluids

P.1  Thermal and caloric equations of state

The systematic development of the thermodynamic theory and its applications begins in Chap. 1 of this book. Some of the applications concern ideal gases, notably air. Others concern nearly incompressible fluids, notably water. Therefore it is appropriate to have the equations for ideal gases and incompressible fluids available at the outset. There are two of them, the thermal equation of state and the caloric one.

The equations of state of ideal gases and of incompressible liquids are the results of the earliest researches in the field of thermodynamics. Their best-known pioneers are Robert BOYLE (1627-1691), Edmé MARIOTTE (1620-1684), Joseph Louis GAY-LUSSAC (1778-1850), James Prescott JOULE (1818-1889) and William THOMSON (Lord KELVIN, 1824-1907) and their work is nowadays a popular subject of the physics curricula in high schools.

Therefore in this somewhat advanced – or intermediate – book on thermodynamic we feel that we may assume those equations as known. We just list them in order to introduce notation and for future reference.

- **Ideal gases**

  The **thermal equation of state** relates the pressure \( p \) of the gas to the mass density \( \rho \) and the absolute temperature \( T \)

  \[
  p = \rho \frac{R}{M} T, \quad \text{where} \quad R = 8.314 \frac{1}{\text{molK}}, \quad \text{and} \quad M = \frac{m}{m_0} \frac{g}{\text{mol}}
  \]

  denote the universal ideal gas constant and the molar mass, respectively; \( m \) is the atomic mass of the gas, and \( m_0 \) is a reference mass – nowadays \( 1/12 \) of the mass of the most common carbon atom, the \( ^{12} \text{C} \) isotope, so that \( m_0 = 1.67 \cdot 10^{-27} \text{g} \) holds.

  The **caloric equation of state** relates the specific internal energy \( u \) to the mass density and temperature

  \[
  u = z \frac{R}{M} (T - T_R) + u_R \quad \text{where} \quad z = \begin{cases} 3/2 & \text{one} - \text{atomic gas} \\ 5/2 & \text{two} - \text{atomic gas} \\ 3 & \text{more} - \text{atomic gas} \end{cases}
  \]

  For ideal gases \( u \) is independent of \( \rho \), and it contains an arbitrary additive constant \( u_R \), representing the internal energy at an arbitrary reference temperature \( T_R \) which is usually chosen as 25°C, or 298 K.

- **Incompressible fluid**

  Incompressibility means

  \[
  \rho = \text{const.}
  \]
The mass density is independent of either pressure or temperature. For water, which is incompressible to a good approximation, the value of $\rho$ is $10^3\, \text{kg/m}^3$.

The caloric equation of state reads
\[ u = c(T - T_R) + u_R, \quad (P.4) \]
where $c$ is the specific heat. For water we have approximately $c = 4.18\, \text{kJ/kgK}$ but, indeed, $c$ depends weakly on temperature, a fact which we often ignore.

P.2 “mol”

The “mol” – appearing in Section (P.1) as a unit – is a unit for the number of atoms or molecules. By (P.1), the mass of all atoms per mol is $M = \frac{m}{\text{mol}}$ and therefore the number of atoms per mol is equal to
\[ A = \frac{M}{m} = \frac{1}{\text{mol}}, \quad \text{or} \quad A = 6.023 \times 10^{23} \cdot \frac{1}{\text{mol}}. \quad (P.5) \]
This number is called AVOGADRO’s number and most often denoted by $A$. One mol of all substances contains that same number of particles.

For a body of mass $m$, volume $V$ and particle number $N$ we may write
\[ \rho = \frac{m}{V} = \frac{Nm}{V}, \]
if the density is homogeneous throughout the body. In an ideal gas the thermal equation of state may then be expressed as
\[ pV = N\left(R\frac{m_0}{\text{mol}}\right)T, \quad \text{and with the Boltzmann constant} \quad k = R\frac{m_0}{\text{mol}} = 1.38 \times 10^{-23} \, \text{J/K} \]
\[ pV = NkT \quad (P.6) \]

This implies AVOGADRO’s law: Equal volumes of different gases at the same pressure and temperature contain equally many particles.

The mol as a unit carries all the potential for confusion as any unit for a dimensionless quantity does. Physicists and most engineers would prefer to carry on without using the mol, but chemists and chemical engineers insist on it. And so the mol is a unit by international agreement along with meter, second, Newton, Kelvin, etc.

The approximate molar masses of a few common substances are as follows
\[ \text{H : 1, O : 16, N : 14, C : 12, Ar : 40, Cl : 35.5, Na : 23; all in } \frac{\text{g}}{\text{mol}} \quad (P.7) \]

Air is a mixture that behaves, under normal conditions, like an ideal gas. It consists of
\[ 78.02\, \% \text{ N}_2, \ 20.95\, \% \text{ O}_2, \ 0.94\, \% \text{ Ar}, \ 0.03\, \% \text{ CO}_2, \quad (P.8) \]
so that the mean mass of an “air molecule” is:
\[ m_{av} = 0.7808 \, m_{\text{N}_2} + 0.209 \, m_{\text{O}_2} + 0.0094 \, m_{\text{Ar}} + 0.0003 \, m_{\text{CO}_2} = 28.96 \, m_0. \quad (P.9) \]

* The percentages in (P.8) are “volume percent.” Before mixing – under the pressure $p$ and temperature $T$ – the constituents occupy 0.7808, 0.209, 0.0094, and 0.0003 parts of the volume of the air after mixing.
Robert Boyle, son of an Irish nobleman took a strong interest in the then new natural philosophy. He worked on chemistry and physics and repeated some of Galileo’s and Guericke’s experiments. He was the first chemist to produce a gas other than air, namely hydrogen, by treating some metals with acids; but he did not name the gas. His contribution to thermodynamics is Boyle’s law: In a gas at constant temperature the volume is inversely proportional to pressure.

Boyle was a zealous religious advocate – he had met God in a particularly intense thundersorm while traveling in Switzerland – and in his lectures he defended Christianity against “notorious infidels, namely atheists, theists, pagans, jews and muslims.”

Edmé Mariotte was as devout as Boyle. He was in fact a priest and Prior of St. Martin sous Beaune. He rediscovered Boyle’s law and he extended it by noting that, at constant pressure, the volume of a gas grows with temperature \( t \). Boyle had not made that observation or, anyway, he did not mention it.

In that early age of natural science most scientists did not limit their attention to a single field of research and so Mariotte was also a keen meteorologist and a keen physiologist. He discovered the circulation of the earth’s water supply and the “blind spot” of the eye.

Joseph Louis Gay-Lussac, about 100 years later than Mariotte, noticed that for a given pressure the volume of a gas is proportional to \( 273°C + t \). This relation is also known as Charles’s law, but Gay-Lussac found out a little more: The factor of proportionality is equal for all gases. Gay-Lussac’s and Charles’s findings foreshadowed the existence of a minimal temperature at \( t = -273°C \). Also Gay-Lussac found that gases combine chemically in simple volume proportions; thus he complemented Dalton’s earlier observation according to which many chemical processes – between any constituents – combine by simple mass proportions.

In 1804 Gay-Lussac ascended to a height of 6 km (!) in a hot air balloon in an effort to determine changes of atmospheric pressure and temperature with height. He married a shop assistant when he caught her reading a chemistry book below the counter. Gay-Lussac is also known for his work on alcohol-water mixtures, which led to the “degrees Gay-Lussac” that were used in many countries to measure, classify, and tax alcoholic beverages.
William Thomson (Lord Kelvin since 1892) completed the thermal equation of state of gases by suggesting the absolute temperature scale whose origin is put at $t = -273°C$ and whose degrees we call K in honor of LORD KELVIN. He accompanied the development of thermodynamics with deep interest and intelligent suggestions for more than half a century, and he promoted Joule, and made Joule’s measurements of the mechanical equivalent of heat known to the scientific community. KELVIN made a fortune through his connection with telegraph transmission through transatlantic cables.

James Prescott Joule was one of the pioneers of the First Law of thermodynamics. He constructed an apparatus in which a weight turned a paddle wheel immersed in water. The water became slightly warmer as a result of friction. Thus he determined the mechanical equivalent of heat: 772 foot-pounds of mechanical work raise the temperature of one pound of water by 1 degree Fahrenheit. In JOULE’s honor the unit of energy is now called 1 Joule. After CLAUSIUS had conceived of the internal energy of ideal gases as independent of density or pressure, JOULE jointly with KELVIN found the Joule-Kelvin effect in air: Expanding air cools very slightly; the cooling is due to the work done to separate the molecules, and it occurs to the extent that the gas is not really ideal. GAY-LUSSAC with his cruder thermometers had missed the cooling effect.

Lorenzo Romano Amadeo Carlo Avogadro, Conte di Quarenga e di Cerreto (1776-1856) came from a distinguished family of lawyers and he himself studied ecclesiastical law and became a lawyer at the age of 16. He was, however, also much interested in physics and chemistry which he studied privately and successfully so that – in 1820 – he became a professor of natural philosophy at the University of Torino. He was able to see a common basis for DALTON’s and GAY-LUSSAC’s observations of simple proportions – by mass and volume, respectively – in chemical reactions and he concluded that equal volumes of different gases contain equally many molecules. This became known as AVOGADRO’s law. Nowadays it is a simple corollary of the thermal equation of state.

P.4 An elementary kinetic view of the equations of state for ideal gases; interpretation of pressure and absolute temperature

We consider a monatomic ideal gas at rest in a rectangular box. The particle number density is $n = N/V$, and we assume $n$ to be so small that the interaction forces between the molecules are negligible. The pressure on the walls results
from the incessant bombardment of the walls by the atoms – at a rate of $10^9$ collisions per second – and we present a strongly simplified model.

$-p \, dA$ is the force of the wall element $dA$ on the gas. This force must be equal to the change of momentum of the atoms which hit $dA$ in the time interval $dt$. The change of momentum is calculated as follows: For simplicity we assume that all atoms have the same speed and that $1/6$ of them fly in the 6 directions perpendicular to the walls. The momentum change of one atom on the wall element $dA$ is then $-2mc$, cf. Fig. P1, and per time interval we will have $c \, dA \, n/6$ such impacts on $dA$. This is to say that all atoms in the cylindrical volume $c \, dt \, dA$ collide with the wall provided they fly forward toward $dA$. Their momentum change is equal to

$$(-2mc)(c \, dt \, dA) = -\frac{1}{3}c^2 \, dA.$$ 

This expression must be equal to $-p \, dA$ and we obtain

$$p = \rho \frac{1}{3}c^2.$$ 

**Fig. P1** Atomic interpretation of the pressure in an ideal gas

Comparison with the thermal equation of state provides

$$\frac{R}{M}T = \frac{1}{3}c^2 \quad \text{or} \quad \frac{3}{2}kT = \frac{m}{2}c^2,$$  

so that the temperature is a measure for the kinetic energy of the atoms.

The energy density $\rho u$ of the model gas is obviously also related to the atomic kinetic energy. We have

$$\rho u = n \frac{m}{2}c^2 = \rho \frac{3}{2} \frac{R}{M}T.$$  

This compares well with the caloric equation of state (P.2) for a monatomic gas. To be sure, $T_R$ must be set to zero to make the analogy complete, and $u_R$ must be zero as well, so that an atom at rest is assigned the energy zero.
The simple model for a gas described above was first introduced by Daniel BERNOULLI (1700-1782). He belonged to a family of eminent mathematicians. His father Johann and his uncle Jacob were both professors, and they knew that there was no money in mathematics. Therefore Daniel was destined to become a physician. But the genes were stronger and he drifted to mathematics during his life. His work on the kinetic theory of gases was largely ignored and the kinetic theory had to be reinvented – and improved – in the nineteenth century, a hundred years after Bernoulli. Daniel is also the author of the Bernoulli equation of fluid mechanics which we shall learn about in Paragraph 1.4.5.

In the eighteenth century scientific academies used to offer awards for the solution of certain unsolved mathematical or physical problems, and Daniel Bernoulli won several of them. In one of those he competed with his father. They both won and had to share the award money. It is said that this event made Johann Bernoulli break off relations with his son.

The equations (P.10) and (P.11) remain valid for more sophisticated gas models, except that in those models \( c \) must be replaced by the mean speed \( \bar{c} \) of the atoms. The deviation of the caloric equation (P.11) from (P.2) for two- and more-atomic molecules is due to the fact that molecules can store energy in rotational motion.

A noteworthy consequence of (P.10) is the value of the (mean) speed of atoms. For helium with \( M \approx 4 \frac{g}{\text{mol}} \) and \( T = 300 \text{ K} \) the speed equals \( \bar{c} = 1360 \ \frac{m}{s} \). For heavier atoms it is smaller. The speed decrease is inversely proportional to \( \sqrt{M} \), so that argon atoms with \( M \approx 40 \frac{g}{\text{mol}} \) move only about \( 1/3 \) as fast as helium atoms.
1 Objectives of thermodynamics and its equations of balance

1.1 Fields of mechanics and thermodynamics

1.1.1 Mass density, velocity, and temperature

During a process the mass density, the velocity, and the temperature of a fluid are, in general, not homogeneous in space, nor are they constant in time. Therefore mass density, velocity, and temperature are called time-dependent fields.

Fluid mechanics proposes to calculate the fields of mass density $\rho(x_i, t)$, and velocity $w_j(x_i, t)$ in a fluid. Thermodynamics proposes to calculate the fields of mass density $\rho(x_i, t)$, velocity $w_j(x_i, t)$, and temperature $T(x_i, t)$ in the fluid. Therefore thermodynamics is more accurate than fluid mechanics: In addition to the motion of the fluid and its inertia, it takes into consideration how “hot” the fluid is.

On the interface between two bodies – the fluid and the wall of the container (say) – the temperature is continuous. This property defines temperature, it is the basis of all measurements of temperature by contact thermometers, and it is often referred to as the Zeroth Law of Thermodynamics.*

Most thermometers rely on the thermal expansion of the thermometric substance, often mercury. In this book we shall usually employ the Celsius scale – or centigrade scale – but often also the absolute or Kelvin scale. Both scales use the same degree of temperature such that melting ice and boiling water at normal pressure differ by 100 degrees. The values of temperature of these fix points are 0°C and 100°C, or 273.15K and 373.15K, respectively.

1.1.2 History of temperature

The word temperature is Latin in origin: *temperare* means to mix and, of course, mixing of two fluids of different temperatures is the easiest method to realize intermediate temperatures. Our skin is fairly sensitive to hot and cold in a certain range, but it is not perfect, because it cannot compensate for subjective circumstances. Therefore thermometers were developed in the 17th century. Gianfrancesco Sagredo (1571-1620), a Venetian diplomat and pupil of Galileo Galilei (1564-1642) experimented with a thermometer in the early 17th century and he wondered at his observation that in winter time the air can be colder than ice or snow. Also in a letter to his former teacher Galilei he expressed his surprise that ...

... water from a well is actually colder in winter than in summer, although our senses judge otherwise.

This is a neat example for the subjectivity of our senses. Indeed, if we bring water up from a well in wintertime and stick our hand into it, it feels warm. If we do the same in summertime, the water feels cool.

* By the time when the basic character of the definition of temperature was fully appreciated, the 1st and 2nd Laws of Thermodynamics had already been firmly labeled.
The genius of Galileo GALILEI as a physicist and mechanician is not really reflected in thermodynamics except that GALILEI categorically claimed – in his correspondence with SAGREDO – that he had invented the thermometer. There is some doubt concerning that claim although SAGREDO was enough of a diplomat to accept it. GALILEI immortalized SAGREDO in his famous narrative treatise *Il Dialogo dei Massimi Sistemi* which takes place in the palace of the SAGREDO family and in which SAGREDO plays the role of the intelligent dilettante. He can be seen as the central figure on the frontispiece of the book.

The introduction of scales with universally reproducible fix points ended the early phase of speculation and hapless observation. The most widely used scale today is the centigrade scale with one hundred equal degrees between the temperatures of boiling water and melting ice. This scale was introduced by Anders Cornelius CELSIUS (1701-1744) and Mårten STRÖMER (1707-1770). CELSIUS had counted downwards from boiling water at 0°C to melting ice at 100°C, because he wished to avoid negative temperatures in wintertime. STRÖMER reversed this direction.

Another traditional scale is the Fahrenheit scale, named after Gabriel Daniel FAHRENHEIT (1686-1736), which also uses melting ice (32°F) and boiling water (212°F) as fix points with 180°F in-between. This scale is still used in some countries, notably in the United States of America. The transformation formulae from Fahrenheit temperature (F) to Celsius temperature (C) and vice versa are given by

\[
C = \frac{5}{9}(F - 32) \quad \text{and} \quad F = \frac{9}{5}C + 32.
\]

FAHRENHEIT also wanted to avoid negative temperatures and therefore in his scale the zero point occurs at -17.8°C. This is the freezing point of sea water and FAHRENHEIT may have thought that it surely would never get colder than that.

There are various quaint alternative propositions for fix points, such as • the melting point of butter, • the temperature of a deep cellar and • the temperature in the armpit of a healthy man.

A fairly complete account of the development of the thermometer, of temperature scales, and of fix points is given in the book by W.E. Knowles MIDDLETON* to which we refer the interested reader.

The absolute scale was proposed by William THOMSON (Lord KELVIN). It relies on the existence of a lowest temperature which defines the zero point of the scale. The other fix point is the triple point of water which occurs at 0.01°C or 273.16 K.

1.2 Equations of balance

1.2.1 Conservation laws of thermodynamics

In order to determine the five fields \( \rho(x_i,t) \), \( w_j(x_i,t) \), and \( T(x_i,t) \) we need five field equations, and these are based on the five conservation laws of mechanics and thermodynamics, namely the

- conservation law of mass, or equation of continuity,
- conservation law of momentum, or NEWTON’s Second Law,
- conservation law of energy, or First Law of Thermodynamics.

Mathematically speaking all of these “laws” are balance equations. Therefore we may avoid repetition by formulating a generic equation of balance first and specializing it to specific cases later.

1.2.2 Generic equations of balance for closed and open systems

In general the elements of the surface \( \partial V \) of thermodynamic systems of volume \( V \) move with the velocity \( u_j(x_i,t) \) which, as indicated by the variables \( x_i \) and \( t \), are usually different for each element and may change over time. Consequently the shape, the size and the location of the system will change.

The equation of balance for a generic quantity with the volume density \( \rho \psi \) – i.e. the specific value \( \psi \) per mass – is an equation for its rate of change

\[
\frac{d}{dt} \Psi = \frac{d}{dt} \int_V \rho \psi \, dV .
\]

The equation reads

\[
\frac{d}{dt} \int_V \rho \psi \, dV = - \int_V \rho \psi (w_i - u_i) n_i \, dA - \int_{\partial V} \phi_t \, n_i \, dA + \int_V \rho (\pi + \zeta) \, dV .
\]
other words, it cannot be influenced directly. To be sure, in a conservation law the production vanishes, and it is this very property that defines a conserved quantity.

The system is called closed, if \( w_i = u_i \) holds everywhere on \( \partial V \). Then (1.2) reduces to

\[
\frac{d}{dt} \int_V \rho \psi \, dV = - \int_{\partial V} \phi_i n_i \, dA + \int_V \rho (\pi + \zeta) \, dV . \tag{1.3}
\]

The system is called open and at rest, if \( u_i = 0 \) holds on \( \partial V \). In this case \( V \) is independent of time and we may write for the left hand side in (1.2)

\[
\frac{d}{dt} \int_V \rho \psi \, dV = \int_V \frac{\partial \rho \psi}{\partial t} \, dV \quad \text{to obtain} \tag{1.4}
\]

\[
\int_{\partial V} \frac{\partial \rho \psi}{\partial t} \, dV = - \int_{\partial V} (\rho \psi w_i + \phi_i) n_i \, dA + \int_V \rho (\pi + \zeta) \, dV . \tag{1.5}
\]

By comparison of (1.3) through (1.5) we obtain

\[
\frac{d}{dt} \int_V \rho \psi \, dV = \int_{\partial V} \frac{\partial \rho \psi}{\partial t} \, dV + \int \rho \psi w_i n_i \, dA . \tag{1.6}
\]

\( V \) on the left hand side is the time-dependent closed volume \( V(t) \), while \( V \) on the right hand side is fixed; it is equal to \( V(t_0) \) (say). The relation is known as the Reynolds transport theorem; it is the three-dimensional analogue of the Leibniz rule for the differentiation of a one-dimensional integral between variable limits.

### 1.2.3 Generic local equation of balance in regular points

We recall GAUSS’s theorem for a smooth function \( a(x_k) \). According to this theorem the surface integral of the function \( a(x_k) n_i (x_k) \) over a closed surface is equal to the volume integral over the gradient field \( \frac{\partial a}{\partial x_i} \)

\[
\int_{\partial V} a n_i \, dA = \int_V \frac{\partial a}{\partial x_i} \, dV . \tag{1.7}
\]

If this rule is applied to the surface integral in (1.5) that equation may be written in the form

\[
\int_V \left( \frac{\partial \rho \psi}{\partial t} + \frac{\partial (\rho \psi w_i + \phi_i)}{\partial x_i} - \rho (\pi + \zeta) \right) \, dV = 0 , \tag{1.8}
\]

provided that \( \rho \), \( \psi \), \( w_i \), and \( \phi_i \) are all smooth functions in \( V \). Since (1.8) must hold for all \( V \) – even for infinitesimally small ones – the integrand itself must vanish. Thus in regular points, where the assumed smoothness holds, we obtain the generic equation of balance as a partial differential equation of the form

\[
\frac{\partial \rho \psi}{\partial t} + \frac{\partial (\rho \psi w_i + \phi_i)}{\partial x_i} = \rho (\pi + \zeta) . \tag{1.9}
\]
1.3 Balance of mass

1.3.1 Integral and local balance equations of mass

In a closed system the mass is constant and therefore we have

$$\frac{d}{dt} \int_V \rho \, dV = 0 \, . \tag{1.10}$$

Comparison with the generic equation (1.3) shows that in the case of the mass balance the generic quantities $\psi$, $\phi_i$, $\pi$ and $\zeta$ must be identified as shown in the following table:

<table>
<thead>
<tr>
<th>$\Psi$</th>
<th>$\psi$</th>
<th>$\phi_i$</th>
<th>$\pi$</th>
<th>$\zeta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Mass is a conserved quantity so that $\pi = 0$ holds. Also there is no way to supply mass to a system except through the surface, and this is why $\zeta = 0$ holds. And, obviously, a non-convective mass flux cannot exist on a surface which moves with the mass.

With the assignments of the table the mass balance of an open system at rest reads according to (1.5):

$$\int_V \frac{\partial \rho}{\partial t} \, dV + \int_{\partial V} \rho \omega_i \, n_i \, dA = 0 \, , \tag{1.11}$$

and the local equation (1.9) is reduced to

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho \omega_i}{\partial x_i} = 0 \, . \tag{1.12}$$

1.3.2 Mass balance and nozzle flow

We consider a flow through a nozzle as shown in Fig. 1.1. The flow is assumed to be stationary which is to say that at each fixed point $x_i$ the density and the velocity are constant. Formally this means that $\frac{\partial}{\partial t} = 0$ holds.

The dashed line in the figure represents an open volume at rest. It consists of two cross-sections, $A^I$ and $A^II$, and the mantle surface $A^M$. The mass balance (1.11) reads

$$\int_{\partial V} \rho \omega_i \, n_i \, dA = 0 \, . \tag{1.13}$$

$\omega_i$ is perpendicular to $n_i$ on the mantle so that on that surface $\omega_i n_i = 0$ holds, which means that the mantle does not contribute in (1.13). Thus the equation reduces to

$$\int_{A^I} \rho \omega_i \, n_i \, dA + \int_{A^II} \rho \omega_i \, n_i \, dA = 0 \, . \tag{1.14}$$
In particular, if we assume one-dimensionality of the flow, meaning that $\rho$ and $w_1$ are homogeneous on a cross-section, we obtain from (1.14)

$$\left(\rho w_1 A\right)^I = \left(\rho w_1 A\right)^{II},$$

(1.15)
since on $A^I$ the normal vector equals $(-1, 0, 0)$, while on $A^{II}$ it reads $(1, 0, 0)$. Thus the mass transfer rate

$$\dot{m} = \rho w_1 A$$

(1.16)
is equal in magnitude for all cross-sections: In general $\rho$, $w_1$, and $A$ are all different for the cross-sections. The product $\rho w_1 A$, however, is a constant. It seems that this property has given rise to the name continuity equation for the mass balance, an expression which is often used in fluid mechanics.

### 1.4 Balance of momentum

**1.4.1 Integral and local balance equations of momentum**

NEWTON’s law of motion states that the momentum $\int_V \rho w_j dV$ of a closed system is changed by the forces acting on the system. These forces are of two types

i.) stress forces or tractions on the surface $\int_{\partial V} t_j dA = \int_{\partial V} t_{ji} n_i dA$

ii.) body forces $\int_V \rho f_j dV$.

$t_j dA$ is the $j$-component of the stress force on the surface element $dA$. The element is equilibrated by the forces $t_{j1} dA_1$ and $t_{j2} dA_2$, cf. Fig. 1.2. Thus, by $dA_1 = dA \cos \alpha$ and $dA_2 = dA \sin \alpha$ we have

$$t_j = t_{j1} \cos \alpha + t_{j2} \sin \alpha = t_{ji} n_i.$$

![Fig. 1.1 Nozzle flow](image-url)
$t_{ji}$ is called the stress tensor. The figure illustrates the significance of the components $t_{ji}$ albeit – for simplicity – only in a two-dimensional case.

In general the stress tensor $t_{ji}$ has nine different components, while the stress force has only three. It is thus clear that the stress tensor $t_{ji}$ at some place cannot be determined by the stress force $t_j$ at that place; we need the stress force on the whole surface. In most fluids – and always in this book – the stress tensor is symmetric so that $t_{ji} = t_{ij}$ holds, and then it has six independent components. Exceptions are fluids with an intrinsic spin, such as liquid crystals.

\[ f_j = (0, 0, -g), \text{ where } g = 9.8067 \frac{\text{m}}{\text{s}^2} \text{ is the gravitational acceleration.} \]

Thus NEWTON’s law of motion for a closed system may be written as

\[ \frac{d}{dt} \int \rho \, w_j \, dV = \int t_{ji} \, n_i \, dA + \int \rho \, f_j \, dV. \quad (1.17) \]

It has the form of an equation of balance for a closed system and the comparison with the generic equation (1.3) leads to the following assignments.

<table>
<thead>
<tr>
<th>$\Psi$</th>
<th>$\psi$</th>
<th>$\phi_i$</th>
<th>$\pi$</th>
<th>$\zeta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>momentum</td>
<td>$\rho w_j$</td>
<td>$-t_{ji}$</td>
<td>$0$</td>
<td>$f_j$</td>
</tr>
</tbody>
</table>

The production density of momentum vanishes, because momentum is a conserved quantity, i.e. in the absence of forces – on the surface and within the body – the momentum is constant.

With the assignments of the table we obtain for an open system at rest

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* The effect of gravitation on a gas or on a vapor may often be neglected because their densities are small.
1.4.2 Pressure

In a fluid at rest, or with a homogeneous velocity field, the stress force \( t_{ji} n_i \, dA \) on an area element \( dA \) is perpendicular to the element for all orientations of the element. This means that
\[
 t_{ji} n_i = -p \, n_j
\]  
holds for all \( n_k \). \( p \) is called the pressure. By setting \( n_i = (1,0,0) \), \( n_i = (0,1,0) \), and \( n_i = (0,0,1) \) we conclude that the stress tensor for the fluid has the form
\[
 t_{ji} = -p \, \delta_{ji} \,, \quad \text{where} \quad \delta_{ji} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} ,
\]  
and we say that the stress tensor is isotropic. The minus sign in (1.20) and (1.21) is due to a convention by which the force of a container wall on the fluid is considered positive. Thus obviously \( p \, dA \) is the force exerted by the fluid on the element \( dA \) of the wall.

If the velocity field of the fluid is not homogeneous so that velocity gradients exist, the stress tensor does have off-diagonal elements and its diagonal components may be different. We say that \( t_{ji} + p \delta_{ji} \) – if unequal to zero – represents the viscous forces in a fluid.

1.4.3 Pressure in an incompressible fluid at rest

With \( w_j = 0 \), \( t_{ji} = -p \delta_{ji} \), and \( f_j = (0,0,-g) \) the local balance of momentum (1.19) reduces to the three equations
\[
 \frac{\partial p}{\partial x_1} = 0 , \quad \frac{\partial p}{\partial x_2} = 0 , \quad \frac{\partial p}{\partial x_3} = -\rho g .
\]  
Hence \( p \) depends only on \( x_3 \) and – since \( \rho = \text{const} \) holds in an incompressible fluid – we have
\[
 p(x_3) = p_0 - \rho \, g \, x_3 ,
\]  
where \( p_0 \) is the pressure at \( x_3 = 0 \). Therefore the pressure increases linearly with increasing depth. In water with \( \rho = 10^3 \frac{\text{kg}}{\text{m}^3} \) the pressure increases by 1 bar roughly for every 10 meters of depth.
1.4.4 History of pressure and pressure units

Evangelista TORRICELLI (1608-1647) was GALILEI’s last pupil and he was given the problem to investigate the function of a suction pump. Fig. 1.3 shows a sketch of such a pump. When the piston is lifted, the water below the piston rises along with the piston. This phenomenon was explained at that time by the so-called *horror vacui*, the perceived horror of nature of an empty space. Indeed, if the water did not follow, a vacuum would develop beneath the piston. And yet, water could not be raised by more than about 10 m in this manner and, if that was attempted, a vacuum *did* appear below the piston.

TORRICELLI solved the problem. He argued that air has weight and this weight pushes on the free surface of the water everywhere adjacent to the pump. When the piston is raised, the air pressure pushes the water into the cylinder of the pump through the valve. This works until the pressure of the lifted water equals the pressure of the air.

TORRICELLI tested his theory by filling a pipe of a height of 1 m with mercury and stuck the open end vertically into a water basin. Mercury has a larger density than water – \( \rho_{\text{Hg}} = 13.595 \text{ g/cm}^3 \) – and, indeed, some mercury flowed out of the pipe but a column of roughly the height \( H_{\text{Hg}} = 760 \text{ mm} \) remained. Above the mercury column an almost empty space had formed – now called a TORRICELLI vacuum – filled only with a minute amount of mercury vapor.

From this observation the maximum height of the water column in a suction pump could be calculated. If mercury and water exert the same pressure, (1.23) implies \( \rho_{\text{Hg}} H_{\text{Hg}} = \rho_{\text{H}_2\text{O}} H_{\text{H}_2\text{O}} \), hence \( H_{\text{H}_2\text{O}} = 10.33 \text{ m} \).

\[ \rho_{\text{Hg}} H_{\text{Hg}} = \rho_{\text{H}_2\text{O}} H_{\text{H}_2\text{O}} \]

The weight of the mercury column of 760 mm height – or of water with 10.33 m height – must be equal to the weight of air on the same cross-section.

For a rough estimate of the thickness of the atmospheric shell of the earth one may assume that the density of air is independent of height and equal to the value \( \rho_{\text{air}} = 1.293 \text{ kg/m}^3 \) at the surface. In that way \( H_{\text{air}} \) would follow from

\[ \rho_{\text{Hg}} H_{\text{Hg}} = \rho_{\text{H}_2\text{O}} H_{\text{H}_2\text{O}} \] as \( H_{\text{air}} = 8000 \text{ m} \).

Although the assumption of a homogeneous air density is bad, the estimate shows that the atmosphere is quite thin, at least compared to the radius of the earth.