1 Continuous matter

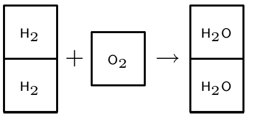
The everyday experience of the smoothness of matter is an illusion. Since the beginning of the twentieth century it has been known with certainty that matter is composed of microscopic atoms and molecules, responsible for the macroscopic properties of ordinary matter. Long before the actual discovery of molecules, chemists had inferred that something like molecules had to exist, even if they did not know how big they were.

Molecules *are* small — so small that their existence may be safely disregarded in all our daily doings. Although everybody possessing a powerful microscope will notice the irregular Brownian motion of bacteria, it took quite some mental effort and a big step away from the everyday manipulation of objects to recognize that this is a sign that molecules are really there.

Continuum physics deals with the systematic description of matter at length scales that are large compared to the molecular scale. Most macroscopic length scales occurring in practice are actually huge in molecular units, typically in the hundreds of millions. This enormous ratio of scales isolates continuum theories of macroscopic phenomena from the details of the microscopic molecular world. There might in principle be many different microscopic models leading to the same macroscopic physics.

The microscopic world impinges upon the macroscopic almost only through material constants characterizing the interactions between macroscopic amounts of matter, such as coefficients of elasticity and viscosity. It is of course an important task for material physics to derive the values of these constants, but this task lies outside the realm of continuum physics. It is nevertheless sometimes instructive to consider the underlying atomic or molecular structure in order to obtain a qualitative understanding of the origin of macroscopic phenomena and of the limits to macroscopic continuum descriptions.

1.1 Molecules



The meaning of a chemical formula.

Chemical reactions such as $2H_2 + O_2 \to 2H_2O$ are characterized by simple integer coefficients. Two measures of hydrogen plus one measure of oxygen yield two measures of water without anything left over of the original ingredients. What are these measures? For gases at the same temperature and pressure, it is simply the volume, so that for example two liters of hydrogen plus one liter of oxygen yield two liters of water vapor, assuming that the water vapor without condensing can be brought to the same temperature and pressure as the gases had before the reaction. Count Avogadro of Italy proposed already in 1811 that the simple integer coefficients in chemical reactions between gases could be explained by the rule that equal volumes of gases contain equal numbers of molecules (at the same temperature and pressure).

Lorenzo Romano Amadeo Carlo Avogadro di Quaregna e Cerretto (1776–1856). Italian philosopher, lawyer, and physicist.

Molecular weight

The various measures do not weigh the same. A liter of oxygen is roughly 16 times heavier than a liter of hydrogen at the same temperature and pressure. The weight of a liter of water vapor must — of course — be the sum of the weights of the ingredients, hydrogen and oxygen, and from the formula it now follows that this becomes roughly $(2 \times 1 + 1 \times 16)/2 = 9$ times the weight of a liter of hydrogen. Such considerations lead early to the introduction of the concept of relative molecular weight or mass in the ratio 1:16:9 (or equivalently 2:32:18) for hydrogen, oxygen and water.

In the beginning there was no way of fixing an absolute scale for molecular mass, because that would require knowledge of the number of molecules in a macroscopic amount of a substance. Instead, a unit, called a *mole*, was quite arbitrarily fixed to be one gram of atomic hydrogen (H). Such a scale is practical for the chemist at work in his laboratory, and the ratios of molecular masses obtained from chemical reactions could then determine the mass of a mole of any other substance. Thus the molar mass of molecular hydrogen (H_2) is 2 grams and that of molecular oxygen (O_2) 32 grams, whereas water has a molar mass of $(2 \times 2 + 1 \times 32)/2 = 18$ grams. This system could be extended to all chemical reactions allowing the determination of molar mass for any substance participating in chemical reactions.

Avogadro's number

We now know that chemical reactions actually describe microscopic interactions between individual molecules built from atoms and that molecular mass is simply proportional to the mass of a molecule. The constant of proportionality was called Avogadro's number by Perrin, who in 1908 carried out the first modern determination of its value from Brownian motion experiments. Perrin's experiments relying on Einstein's recent (1905) theory of Brownian motion were not only seen as a confirmation of this theory but also as the first direct evidence

Jean-Baptiste Perrin (1870–1942), French physicist, received the Nobel prize for his work on Brownian motion in 1926.

for the reality of atoms and molecules. Today, Avogadro's number is *defined* to be the number of atoms in exactly 12 gram of the fundamental carbon isotope ($^{12}\mathsf{C}$), and its value is $N_A = 6.022137(3) \times 10^{23}$ molecules per mole. Notice that in this book, the absolute error on the last digits of a quantity is indicated by means of a parenthesis following the mantissa.

The molecular scale

Consider a substance with mass density ρ and molar mass $M_{\rm mol}$. A mole of the substance occupies a volume $M_{\rm mol}/\rho$, and the volume per molecule becomes $M_{\rm mol}/\rho N_A$. A cube with this volume would have sides of length

$$L_{\rm mol} = \left(\frac{M_{\rm mol}}{\rho N_A}\right)^{\frac{1}{3}} , \tag{1-1}$$

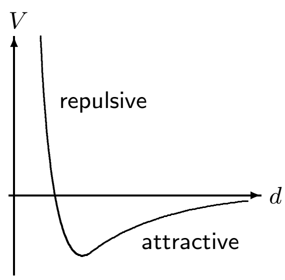
which may be called the *molecular scale*. For iron we get $L_{\rm mol} \approx 0.24$ nm, for water $L_{\rm mol} \approx 0.31$ nm, and for air at normal temperature and pressure $L_{\rm mol} \approx 3.6$ nm. For liquids and solids, where the molecules touch each other, this length is roughly the size of a molecule, whereas in gases it may be much larger. There is a lot of vacuum in a gas.

Molecular forces

Johannes Diederik van der Waals (1837–1923). Dutch physicist, received the Nobel Prize in 1910 for his work on fluids and gases.

Apart from the omnipresent gravitational interaction between all bodies, molecular interactions are entirely electromagnetic in nature, from the fury of a tornado to the gentlest kiss. A deeper understanding of the so-called van der Waals forces acting between neutral atoms and molecules requires quantum theory and falls outside the scope of this book.

Generally, however, the forces between neutral atoms and molecules are short-ranged and barely reach beyond nearest molecular neighbors. They are strongly repulsive if the atoms are forced closer than their natural sizes allow and moderately attractive when they are moved apart a little distance, but farther away they quickly die out. When two molecules are near each other, this tug of war between repulsion and attraction leads to a minimum in the potential energy between the molecules. The state of matter depends, broadly speaking, on the relation between the depth of this minimum, called the binding energy, and the average kinetic energy due to the thermal motion of the molecules.



Sketch of the intermolecular potential energy V as a function of intermolecular distance d. It is attractive at moderate range and strongly repulsive at close distance.

Solids, liquids and gases

In *solid matter* the minimum lies so deep that thermal motion cannot overcome the attraction. Each individual atom or molecule is tied to its neighbors by largely elastic forces. The atoms constantly undergo small-amplitude thermal motion around their equilibrium positions, but as long as the temperature is not so high that the solid melts, they are bound to each other. If external forces are applied, solids may *deform* elastically with increasing force, until they eventually become plastic or even fracture. Most of the work done by external forces in deforming elastic solids can be recovered as work when the forces disappear.

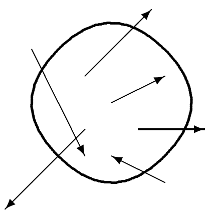
In *fluid matter*, liquids and gases, the minimum is so shallow that the thermal motion of the molecules is capable of overcoming the attractive forces between them. The molecules effectively move freely around between collisions, more so in gases than in liquids where molecular conglomerates may form. External forces make fluids *flow* — in liquids a kind of continual fracturing — and a part of the work done by such forces is dissipated into random molecular motion, or heat, which cannot directly be recovered as work when the forces cease to act.

1.2 The continuum approximation

Whether a given number of molecules is large enough to warrant the use of a smooth continuum description of matter depends on the precision desired. Since matter is never continuous at sufficiently high precision, continuum physics is always an approximation. But as long as the fluctuations in physical quantities caused by the discreteness of matter are smaller than the desired precision, matter may be taken to be continuous. Continuum physics is, properly viewed, a branch of statistical physics with all macroscopic quantities such as mass density and pressure being understood as averages over microscopic molecular variables.

Luckily, it is only rarely necessary to exploit this connection. In a few cases, such as in the example given just below, it is useful to look at the molecular underpinnings of continuum physics. In doing so, we shall use the simplest "molecular" description possible. A quite general meta-law of physics says that the physical laws valid at one length scale are not very sensitive to the details of what happens at much smaller scales. Without this law, physics would in fact be impossible, because we never know what lies below our currently deepest level of understanding.

Precision and continuity



In a gas the molecules move rapidly in and out of a small volume with typical velocities of the order of the speed of sound.

Suppose that we want to determine the mass density $\rho = mN/V$ of a gas to a certain relative precision r, say $r = 1$ %, by counting the number of molecules N of mass m in a small volume V. Due to random motion of the gas molecules, the number N will fluctuate and yield a different value if measured again. In order for the relative precision on the density to be r, we must require that the typical fluctuation ΔN in the number of molecules obeys $\Delta N \lesssim rN$. If the time between measurements is large compared to the time between atomic collisions, the molecules in the volume V will all be replaced by other molecules, and be essentially a random collection of molecules from the gas at large. Since the fluctuation in such a random process is of order $\Delta N \approx \sqrt{N}$ (see fig. 1.1 and problem 1.1), the condition becomes $\sqrt{N} \lesssim rN$ or $N \gtrsim r^{-2}$. The linear dimension of the volume occupied by the smallest allowed number of molecules is $L_{\text{min}} \approx N^{1/3} L_{\text{mol}} \approx r^{-2/3} L_{\text{mol}}$. At a precision level of $r = 1$ %, the smallest

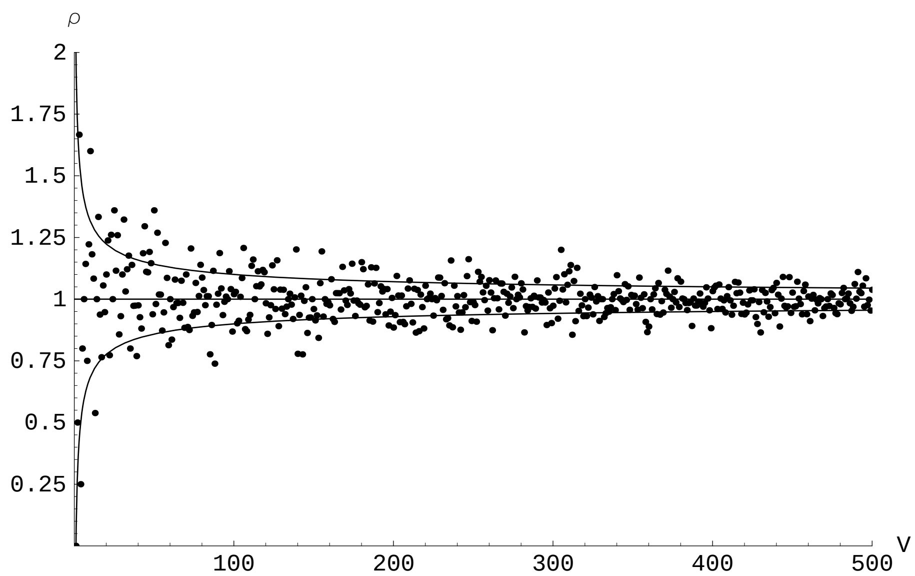
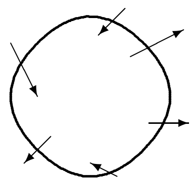


Figure 1.1: *Measured density as a function of volume size. A 3-dimensional volume of size* $20 \times 20 \times 20 = 8000$ *is randomly filled with as many molecules. On the average each of the 8000 unit subvolumes should receive a single molecule, corresponding to an average density of* $\rho = 1$. *The plot shows the actual density of a random collection of* V *subvolumes as a function of* V. *The fully drawn curves indicate the magnitude of the expected fluctuations,* $\rho = 1 \pm 1/\sqrt{V}$.

volume under consideration should contain more than 10^4 molecules, and the dimensions of such a volume must be greater than $L_{\rm min} \approx 22 L_{\rm mol}$.

In a solid, the molecules do not move around much but oscillate instead randomly around more or less fixed positions. At the surface of the volume, V, there is of the order of $N^{2/3}$ molecules that may randomly be in or out of the volume when measurements are done. The corresponding fluctuation in N becomes $\Delta N \sim \sqrt{N^{2/3}} = N^{1/3}$, and we must require $N \gtrsim r^{-3/2}$ in order to obtain the desired precision. For $r = 1\%$, the smallest volume must contain more than 1000 molecules and be of linear dimension greater than $L_{\rm min} \sim r^{-1/2} L_{\rm mol} \approx 10 L_{\rm mol}$.



In a solid the molecules tend to oscillate around fixed positions which gives rise to some fuzziness at the surface of a small volume.

From these two examples we learn that there is a minimal continuum length scale, $L_{\rm min}$, which separates the microscopic description from the macroscopic. This scale must satisfy the inequalities

$$L_{\rm mol} \ll L_{\rm min} \ll L \; , \tag{1-2}$$

where L is a typical length scale of the physical system, for example the size of a cup of water or the size of a hurricane. The continuum scale will always depend on the relative precision r to which our continuum description should apply. In the examples above we found $L_{\rm min} \sim r^{-\alpha} L_{\rm mol}$ with $\alpha = 2/3$ for a gas and $\alpha = 1/2$ for a solid. Since $r^{-\alpha}$ diverges for $r \to 0$, we have obtained a quantitative substantiation of the claim that it is impossible to maintain a continuum description to arbitrarily small relative precision.

Other conditions

There may be further conditions on the continuum length scale. A smooth continuum description requires that molecules interact with each other in order to "iron out" strong differences in velocities. If there were no interactions, a molecule with a given velocity would keep on moving with that velocity forever. In a gas the *mean free path* λ between collisions is a measure of the scale at which this smoothing occurs. At normal temperature and pressure the mean free path is typically about 100 times larger than the molecular size, *i.e.* $\lambda \approx 30$ nm, and the continuum length scale should also be chosen much larger than that.

Material particles

In continuum physics we shall generally permit ourselves to speak about *material particles* as the smallest objects that may consistently be considered part of the continuum description within the required precision. A material particle will always contain a large number of molecules but may in the continuum description be thought of as infinitesimal or point-like.

Although we usually shall think of material particles as being of the same kind in different types of matter, they are in fact quite different. In solids, we may with some reservation think of *solid particles* as containing a fixed number of molecules, whereas in fluids and especially in gases we should not forget that the molecules making up a *fluid particle* at a given instant will shortly after be replaced by other molecules.

1.3 Continuum mechanics

Sir Isaac Newton (1642–1727). English physicist who founded classical mechanics on three famous laws.

In Newtonian mechanics the basic material object is a point particle possessing various mechanical properties, such as position, velocity, acceleration, mass, momentum, angular momentum, and kinetic energy. Newton's second law is *the* fundamental equation of motion and states that mass times acceleration equals force for each point particle. Since the force on a particle can depend on the positions and velocities of the particle itself and other particles, as well as on external parameters, the dynamics of a collection of particles becomes a web of coupled second order differential equations in time.

Macroscopic bodies

Even if macroscopic bodies *are* huge collections of atoms and molecules, it is completely out of question to solve the resulting web of differential equations. In addition there is the problem that molecular interactions are quantum mechanical in nature, and Newtonian mechanics strictly speaking does not apply at the atomic level. This knowledge is, however, relatively new and has as mentioned earlier some difficulty in making itself apparent at the macroscopic level. So even if quantum mechanics rules the world of atoms, its special character is rarely amplified to macroscopic proportions.

In *continuum mechanics* a macroscopic body is seen as a huge collection of tiny material particles all obeying Newton's second law. Each particle occupies a little volume, and the density of a physical quantity such as mass is calculated by dividing the mass of a particle with its volume. Provided the mass density only varies a little between neighboring particles, it may at any instant of time be replaced by a smooth ("continuous") function of the spatial position. In the mathematical limit, the material particles are taken to be truly infinitesimal and all physical properties of the particles as well as the forces acting on them are described by smooth functions of the spatial position and time.

Fields

Continuum physics is therefore a theory of *fields*. Mathematically, a field f is simply a real-valued function $f(x, y, z, t)$ of spatial coordinates x, y, z, and of time t, representing the value of a physical quantity in this point of space at the given time, for example the mass density ρ. Sometimes a collection of such functions is also called a field and the individual real-valued members are called its components. Thus, the most fundamental field of continuum mechanics, the velocity field $\boldsymbol{v} = (v_x, v_y, v_z)$, has three components, one for each of the coordinate directions.

Besides fields characterizing the state of the material, such as mass density and velocity, it is convenient to employ fields that characterize the forces acting on and within the material. The gravitational acceleration field $\boldsymbol{g}$ is a *body force* field, which penetrates bodies from afar and acts on their mass. Some force fields are only meaningful for regions of space where matter is actually present, as for example the pressure field p, which acts across the imagined contact surfaces that separate neighboring parts of a fluid at rest. Pressure is, however, not the only *contact force*. For fluids in motion, for solids and materials in general, contact forces are described by the 9-component stress field, $\boldsymbol{\sigma} = \{\sigma_{ij}\}$, which is a 3×3 matrix field with rows and columns labelled by coordinates: $i, j = x, y, z$.

Mass density, velocity, gravity, pressure, and stress are the usual fields of continuum mechanics and will all be properly introduced in the chapters to come. Some fields are thermodynamic, like the temperature T. Others, for example the electric charge density ρ_c and current density $\boldsymbol{j}_c$, characterize the electromagnetic state of matter, whereas electromagnetic forces are mediated by the electric field strength $\boldsymbol{E}$ and the magnetic field strength $\boldsymbol{B}$. The gravitational field $\boldsymbol{g}$ and the electromagnetic fields determine the forces that would act on a material particle at any point of space, independently of whether there is an actual particle present there or not. These fields are thought to exist even in regions of space completely devoid of matter.

There are also fields that refer to material properties, for example the coefficient of shear elasticity, μ, of a solid and the coefficient of shear viscosity, η, of a fluid. Such fields are usually constant within homogeneous bodies, *i.e.* independent of space and time, and are mostly viewed as material constants rather than true fields.

Field equations

Like all physical variables, fields evolve with time according to certain dynamical laws, called *field equations*. In continuum mechanics, the equation of motion for the velocity field descends directly from Newton's second law applied to every material particle. Other field equations are not directly related to Newtonian particle dynamics. Mass conservation which is all but trivial and most often tacitly incorporated in elementary mechanics turns into an equation of motion for the mass density when applied to continuous matter. Still other field equations such as Maxwell's equations for the electromagnetic fields have completely different and non-mechanical origins.

Mathematically field equations are *partial differential equations* in both space and time. This makes continuum mechanics considerably more difficult than particle mechanics where the equations of motion are ordinary differential equations in time. On the other hand, this greater degree of mathematical complexity also leads to a plethora of new and sometimes quite unexpected phenomena.

In some field theories, for example Maxwell's electromagnetism, the field equations are *linear* in the field variables, but this is not the case in continuum mechanics. The *non-linearity* of the field equations, in particular for fluid mechanics, adds a further layer of mathematical difficulty to this subject, making it very different from linear theories. The non-linearity creates dynamic instabilities and gives rise to the chaotic and as yet not fully understood phenomenon of *turbulence*, so well-known from our daily dealings with water and air.

1.4 Is matter *really* discrete or continuous?

Although continuum physics is always an approximation to the underlying discrete atomic level, this is not the end of the story. At a deeper level it turns out that matter is best described by another continuum formalism, relativistic quantum field theory, in which the discrete particles — electrons, protons, neutrons, nuclei, atoms, and everything else — arise as quantum excitations. Relativistic quantum field theory without gravitation emerged in the first half of the twentieth century as *the* basic description of the atomic world, but in spite of its enormous success, it is still not clear how to include gravity.

Just as the continuity of macroscopic materials is an illusion, the quantum field continuum may itself one day become replaced by even more fundamental discrete or continuous descriptions of space, time, and matter. It is by no means evident that there could not be a fundamental length in nature setting an ultimate lower limit to distance and time, and theories of this kind have in fact been proposed. It appears that we do not know, and perhaps will never know, whether matter at its deepest level is truly continuous or truly discrete.

Problems

1.1 Consider a small volume of a gas which is a fraction p of a larger volume containing M molecules. The probability for any molecule to find itself in the small volume may be taken to be p.

a) Calculate the probability that the small volume contains n molecules.

b) Show that the average of the number of molecules in the small volume is $N \equiv \langle n \rangle = pM$.

c) Show that the variance is $\Delta N^2 \equiv \langle (n - \langle n \rangle)^2 \rangle = p(1-p)M \approx N$ for $p \ll 1$.

1.2 Consider a material gas particle containing N identical molecules. Write the velocity of the n-th molecule as $\boldsymbol{v}_n = \boldsymbol{v} + \boldsymbol{u}_n$ where $\boldsymbol{v}$ is the center of mass velocity and $\boldsymbol{u}_n$ is a random contribution from thermal motion. It may be assumed that the average of the random component of velocity vanishes $\langle \boldsymbol{u}_n \rangle = \mathbf{0}$, that all random velocities are uncorrelated, and that their fluctuations are the same for all particles $\langle \boldsymbol{u}_n^2 \rangle = v_0^2$. Show that the average of the center of mass velocity for the fluid particle is $\langle \boldsymbol{v}_c \rangle = \boldsymbol{v}$ and that its fluctuation due to thermal motion is $\Delta v_c = v_0/\sqrt{N}$.

