

## Part I

# Introduction



# 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 the material world 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.

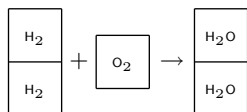
Continuum physics deals with the systematic description of matter at length scales that are large compared to the molecular scale. Most macroscopic length scales occurring in practice are actually huge in molecular units, typically in the hundreds of millions. This enormous ratio of scales isolates continuum 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.

This chapter paints in broad outline the transition from molecules to continuous matter, or mathematically from particles to fields. It is emphasized that the macroscopic continuum description must necessarily be of statistical nature, but that random statistical fluctuations are strongly suppressed by the enormity of the number of molecules in any macroscopic material object. The central theme of this book is the recasting of Newton's laws for point particles into a systematic theory of continuous matter, and the application of this theory to the wealth of exotic and everyday phenomena of the macroscopic material world. For completeness, a short review of Newton's laws is presented in appendix B.

## 1.1 Molecules

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 the physics of materials to derive the values of these constants, but this task lies outside the realm of continuum physics. In 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.

### Molecular weight



*The meaning of a chemical formula.*

Lorenzo Romano Amadeo Carlo Avogadro (1776–1856). *Italian philosopher, lawyer, chemist and physicist. Count of Quaregna and Cerratto. Formulated that equal volumes of gas contain equal numbers of molecules. Also argued that simple gases consist of diatomic molecules.*

Chemical reactions such as  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$  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).

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 ( $\text{H}_2$ ) is 2 grams and that of molecular oxygen ( $\text{O}_2$ ) 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 most direct evidence 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 ( $^{12}\text{C}$ ), and its value is  $N_A = 6.022137(3) \times 10^{23}$  molecules per mole<sup>1</sup>.

## Molecular separation

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

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

which may be called the scale of *molecular separation*. For iron we get  $L_{\text{mol}} \approx 0.24$  nm, for water  $L_{\text{mol}} \approx 0.31$  nm, and for air at normal temperature and pressure  $L_{\text{mol}} \approx 3.6$  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, in fact about 1000 times the volume of matter at normal temperature and pressure.

## Molecular forces

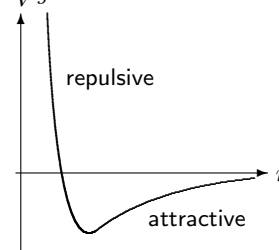
Apart from the omnipresent gravitational interaction between all bodies, molecular interactions are entirely electromagnetic in nature, from the fury of a tornado to the gentlest kiss. A deeper understanding of the so-called van der Waals forces acting between neutral atoms and molecules requires quantum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

<sup>1</sup>In this book the absolute error on the last digits of a quantity is indicated by means of a parenthesis following the mantissa.

Jean-Baptiste Perrin (1870–1942). *French physicist. Received the Nobel Prize for his work on Brownian motion in 1926. He founded several French scientific institutions, among them the now famous “Centre National de la Recherche Scientifique (CNRS)”.*

Johannes Diederik van der Waals (1837–1923). *Dutch physicist. Developed an equation of state for gases, now carrying his name. Received the Nobel Prize in 1910 for his work on fluids and gases.*



*Sketch of the intermolecular potential energy  $V(r)$  as a function of intermolecular distance  $r$ . It is attractive at moderate range and strongly repulsive at close distance.*

relation between the depth of this minimum, called the binding energy, and the average kinetic energy due to the thermal motion of the molecules.

### 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, like thermodynamics, a limit of statistical physics where all macroscopic quantities such as mass density and pressure are understood as averages over essentially infinite numbers of microscopic molecular variables.

Luckily, it is only rarely necessary to exploit this connection. In a few cases, such as in the analysis 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

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,

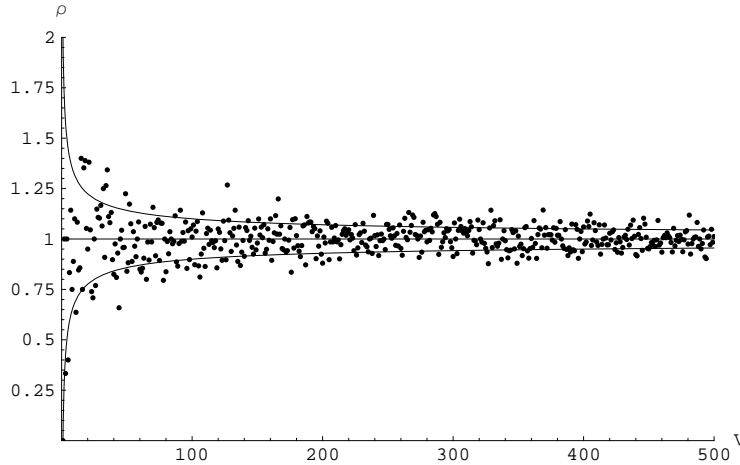


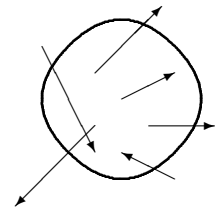
Figure 1.1: Measured density as a function of volume size. A 3-dimensional “universe” consisting of  $20 \times 20 \times 20 = 8000$  cells is randomly filled with as many “molecules”. On average each of the 8000 cells should receive a single molecule, corresponding to a density of  $\rho = 1$ . A “material particle” consisting of  $V$  cells will in general not receive precisely  $V$  molecules, and thus get an actual density that deviates from unity. The plot shows the actual density of a random collection of  $V$  cells as a function of  $V$ . The fully drawn curves,  $\rho = 1 \pm 1/\sqrt{V}$ , indicate the expected fluctuations.

the number  $N$  will fluctuate and yield a different value if measured again. For the relative fluctuation in the density to be at most  $r$  we must require that the typical fluctuation  $\Delta N$  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 an essentially random collection of molecules from the gas at large. Since the fluctuation in such a random process is of order  $\Delta N \approx \sqrt{N}$ , the condition becomes  $\sqrt{N} \lesssim rN$ , or  $N \gtrsim r^{-2}$  (see fig. 1.1 and problem 1.1). The smallest allowed number of molecules,  $N_{\text{micro}} \approx r^{-2}$ , occupies a cubic volume with side length

$$L_{\text{micro}} = N_{\text{micro}}^{1/3} L_{\text{mol}} \approx r^{-2/3} L_{\text{mol}}. \quad (1-2)$$

In liquids and especially in solids the molecules do not move around much but oscillate instead randomly around more or less fixed positions. The density fluctuations in a volume are mainly due to molecules passing in and out of the surface. In problems 1.2 and 1.3 the fluctuations are estimated for a cube and a sphere, resulting in a microscopic length scale of roughly the same form as above, although with an exponent of  $-\frac{1}{2}$  instead of  $-\frac{2}{3}$ .

**Example 1.2.1:** At a precision level of  $r = 1\%$ , the smallest volume under consideration should contain at least  $N_{\text{micro}} \approx 10^4$  molecules, and the linear dimension of such a volume will be greater than  $L_{\text{micro}} \approx 22L_{\text{mol}}$ . For air under normal conditions this comes to about 80 nanometers, while for liquids and solids it is an order of magnitude smaller because of the smallness of  $L_{\text{mol}}$ .



*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.*

## Mean free path

Another condition for obtaining a smooth continuum description, is that molecules should interact with each other 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 solids and liquids where the molecules are closely packed, these interactions take place over a couple of molecular separation lengths and put no further restriction on the microscopic length scale.

In gases there is a lot of vacuum and molecules move freely over long distances. The mean free path between collisions may be estimated by considering a spherical molecule or atom of diameter  $d$  with its center tracing out a straight path through the gas. It will hit any other sphere of the same diameter within a “striking” distance  $d$  from the path, *i.e.* inside a cylinder of diameter  $2d$ . Since there is on average one molecule in each volume  $L_{\text{mol}}^3$ , the distance the original sphere has to move before being sure of hitting another is on average,  $\lambda = L_{\text{mol}}^3/\pi d^2$ . A more careful analysis leads to the following expression for the *mean free path*,

$$\lambda = \frac{L_{\text{mol}}^3}{\sqrt{2} \pi d^2} , \quad (1-3)$$

with an extra factor  $\sqrt{2}$  in the denominator.

For air at normal temperatures we find  $\lambda \approx 113$  nm which is not much larger than the microscopic length scale,  $L_{\text{micro}} \approx 80$  nm (with  $r = 1\%$ ). For dilute gases the mean free path is much larger than the microscopic scale and determines the size of the smallest continuum volumes rather than  $L_{\text{micro}}$ , unless the desired relative precision is very small (see problem 1.5).

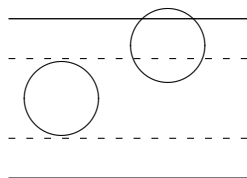
## Macroscopic smoothness

The macroscopic smoothness of the continuum description also depends on the microscopic length scale. If  $L$  denotes the typical macroscopic length scale for major variations in density, the relative density change over the distance  $L_{\text{micro}}$  will typically be of magnitude  $\Delta\rho/\rho \approx L_{\text{micro}}/L$ . Requiring this to be smaller than the measurement precision  $r$ , we must have  $L \gtrsim L_{\text{macro}}$  where

$$L_{\text{macro}} \approx \frac{1}{r} L_{\text{micro}} . \quad (1-4)$$

Any region in which the density varies by a major amount must be larger than  $L_{\text{macro}}$ . Otherwise the continuum description breaks down. With  $r = 1\%$  we find  $L_{\text{macro}} \approx 100L_{\text{micro}}$ . For air under normal conditions this is about 10 micrometers.

Both the micro and macro scales diverge for  $r \rightarrow 0$ , substantiating the claim that it is impossible to maintain a continuum description to arbitrarily small relative precision. The smallness of both length scales for ordinary matter and for reasonable relative precision shows that there is ample room for a smooth continuum description of everyday phenomena. Nanophysics, however, straddles the border between the continuum and particle descriptions of matter, resulting in a wealth of new phenomena outside the scope of classical continuum physics.



A sphere of diameter  $d$  will collide with any other sphere of the same diameter with its center inside a cylinder of diameter  $2d$ .



## 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 collection of molecules, whereas in liquids and 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. If the molecular composition of the material in the environment of a material particle has a slow spatial variation, this incessant molecular game of “musical chairs” may slowly change the composition of the material inside the particle. Such *diffusion* processes driven by spatial variations in material properties lie at the very root of fluid mechanics. Even spatial variations in the average flow velocity will drive momentum diffusion, causing internal (viscous) friction in the fluid.

## 1.3 Newtonian mechanics

In Newtonian mechanics (see appendix B) the basic material object is a point particle with a fixed mass  $m$ . Newton’s second law is *the* fundamental equation of motion, and states that *mass times acceleration equals force*. Mathematically, it is expressed as a second order differential equation in time  $t$ ,

$$m \frac{d^2 \mathbf{x}}{dt^2} = \mathbf{f} , \quad (1-5)$$

where  $\mathbf{x}$  the instantaneous position of the particle, and  $\mathbf{f}$  the force acting on it. In chapter 2 we shall introduce vector calculus to handle quantities like  $\mathbf{x}$  and  $\mathbf{f}$  in a systematic way, but for now any understanding of the meaning of a vector will work fine.

Since the force on any given particle can depend on the positions and velocities of the particle itself and of other particles, as well as on external parameters, the dynamics of a collection of particles becomes a web of coupled ordinary second order differential equations in time. 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.

Sir Isaac Newton (1642–1727). *English physicist and mathematician. Founded classical mechanics on three famous laws in his books “Philosophiæ Naturalis Principia Mathematica” (1687). Newton developed calculus to solve the equations of motion, and formulated theories of optics and of chemistry. He still stands as the greatest scientific genius of all time.*

## Global mechanical quantities

In Newtonian particle mechanics, a “body” is taken to be a fixed collection of point particles, each obeying the second law (1-5). For any body one may define various *global mechanical quantities* which like the total mass are calculated as sums over contributions from each and every particle in the body. Some of the global quantities are *kinematic* such as the total momentum, angular momentum, and kinetic energy. Others are *dynamic* such as the total force, moment of force, and power (total rate of work of all forces). Newton’s second law for the particles leads to three simple relations between the kinematic and dynamic quantities,

- *the rate of change of momentum equals force,*
- *the rate of change of angular momentum equals moment of force,*
- *the rate of change of kinetic energy equals power.*

Even if these laws are not sufficient to determine the dynamics of the body, they represent seven individual constraints on the motion of any system of point particles, independently of how complex it is. In particular they can be taken over in continuum mechanics when exchange of matter between a body and its environment is properly taken into account.

## 1.4 Continuum physics

In *continuum physics* a macroscopic body is seen as a huge collection of tiny material particles, each of which contains a sufficiently large number of molecules to justify a continuum description. Continuum physics does not “on its own” go below the level of the material particles. Although the mass density may be calculated by adding together the masses of all the molecules in a material particle and dividing with the volume occupied by it, this falls strictly speaking outside continuum physics.

In the extreme 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 space and time.

### The field concept

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 time  $t$ , representing the value of a physical quantity in this point of space at the given time, for example the mass density  $\rho$  or  $\rho(x, y, z, t)$ . 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 fluid mechanics, the velocity field  $\mathbf{v} = (v_x, v_y, v_z)$ , 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  $\mathbf{g}$  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 volumes of a fluid at rest. Pressure is, however, not the only *contact force*. For fluids in motion, for solids and more general materials, contact forces are described by the 9-component stress field,  $\boldsymbol{\sigma} = \{\sigma_{ij}\}$ , which is a  $3 \times 3$  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  $T$  and the internal energy density  $u$ . Others, for example the electric charge density  $\rho_c$  and current density  $\mathbf{j}_c$ , characterize the electromagnetic state of matter, whereas electromagnetic forces are mediated by the electric and magnetic field strengths,  $\mathbf{E}$  and  $\mathbf{B}$ . Like gravity  $\mathbf{g}$ , these fields are thought to exist in regions of space completely devoid of matter.

There are also fields that refer to material properties, for example the coefficient of shear elasticity  $\mu$  of a solid and the coefficient of shear viscosity  $\eta$  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 dynamical laws, called *field equations*. In continuum mechanics, the central equation of motion descends directly from Newton's second law applied to every material particle. Mass conservation which is all but trivial and most often tacitly incorporated in particle mechanics turns into an equation of motion for the mass density in 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 fields, but this is not the case in continuum mechanics. The *non-linearity* of the field equations of fluid mechanics adds a further layer of mathematical difficulty to this subject, making it very different from linear theories such as electromagnetism. The non-linearity leads to dynamic instabilities and gives rise to the chaotic and as yet not fully understood phenomenon of *turbulence*, well-known from our daily dealings with water and air.

### Physical reality of force fields

Whereas the mass density only has meaning in regions actually containing matter, and may be defined to be zero in the vacuum, the gravitational field is assumed to exist and take non-vanishing values even in the vacuum. It specifies the force that would be exerted on a unit mass particle at a given point, but the field is assumed to be there even if no particles are present.

In non-relativistic Newtonian physics, the gravitational field has no independent physical meaning and may be completely eliminated and replaced by non-local forces acting between material bodies. The true physical objects appear to be the material bodies, and the gravitational field just a mathematical convenience for calculating the gravitational force exerted by these bodies. There are no independent dynamical equations that tell us how the Newtonian field of gravity changes with time. When material bodies move around or change their mass distributions, the field will change instantaneously with them.

In relativistic mechanics, on the other hand, fields take on a completely different meaning. The reason is that instantaneous action-at-a-distance cannot take place. If matter is moved, the current view is that it will take some time before the field adjusts to the new positions, because no signal can travel faster than light. Due to relativity, fields must travel independently, obey their own equations of motion, and carry physical properties such as energy and momentum. Electromagnetic waves bringing radio and tv signals to us, are examples of force fields thus liberated from their origin. Gravitational waves have not yet been observed directly, but indirectly they have been observed in binary neutron star systems which can only be fully understood if gravitational radiation is taken into account.

Even if we shall not deal with relativistic theories of the continuum, and therefore may consider the gravitational field to be merely a mathematical convenience, it may nevertheless be wise, at least in the back of our minds, to think of the field of gravity as having an independent physical existence. Then we shall have no philosophical problem endowing it with physical properties, even in matter-free regions of space.

### 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 in the fields. Relativistic quantum field theory without gravitation emerged in the first half of the twentieth century as *the* basic description of the subatomic 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** Show that a cube containing  $N = M^3$  smaller cubes of equal size will have  $K = 6M^2 - 12M + 8$  smaller cubes lying on the surface. Estimate the fluctuation  $\Delta N$  when  $N$  molecules in a cube oscillate with amplitude equal to the molecular size.

**1.3** A spherical volume contains a large number  $N$  of molecules. Estimate the number of molecules  $N_S$  situated at the surface and show that the fluctuation in this number is  $\Delta N \approx 6^{1/3} \pi^{1/6} N^{1/3} \approx 2.2N^{1/3}$  when they randomly oscillate with amplitude equal to the molecular size.

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

**1.5** At what precision is the microscopic scale  $L_{\text{micro}}$  equal to the mean free path, when the air density is 100 times smaller than normal.

**1.5** Solving  $L_{\text{micro}} = \lambda$  we get

$$r = (\pi\sqrt{2})^{3/2} \frac{d^3}{L_{\text{mol}}^3} \approx 10 \frac{d^3}{L_{\text{mol}}^3} . \quad (1-6)$$

Under normal conditions  $L_{\text{mol}} \approx 10d$  so  $r = 10^{-2}$ . Since  $L_{\text{mol}}^3 \propto 1/\rho$ , the required precision for the dilute air is 100 times smaller, or  $10^{-4}$ .