Chapter 2
Simple Materials

Abstract In this chapter we are concerned with materials comprising a single type of elementary constituent, in the form of identical atoms or small molecules. These constituents exert forces on one another which decrease with the distance between them. When thermal agitation, which increases with the temperature of the system, is stronger than the interaction forces which tend on the whole to bring the constituent elements together, the matter is in the gaseous state. In this case, the mechanical properties of the material are associated with collisions between molecules and statistical tools can be used to obtain exact relations between the viscosity and the physical characteristics of the gas. When the attractive forces are strong enough compared with thermal agitation, the basic constituents tend to form a compact cluster. This is the liquid state. In this case, our understanding of the relationships between internal forces and the dynamical evolution of such disordered structures in flow remains incomplete. In certain cases, for example, at lower temperatures or higher pressures, the material may become slightly more compact than in the liquid state and arrange itself into an ordered structure. This is the solid state. The material can then be deformed to a certain extent and a direct relationship can be established between the force required and the local interaction forces.

2.1 Introduction

Here we shall be concerned with materials comprising a single type of elementary constituent in the form of identical atoms or small molecules. We thus exclude polymers for the moment. These materials are therefore simple with regard to their composition, containing a single type of element which is not only undeformable but also indestructible under ordinary conditions. It should be said that this is no guarantee of simplicity in rheophysics, since mechanical behaviour does not depend solely on intrinsic characteristics of the constitutive matter. It depends also and above all on the interactions prevailing between these elements, that is, the different types

of forces between them, and on the structure of the material, that is, the relative spatial arrangement of the elements. Regarding structure, the simple materials fall into several main categories, associated with different states of order and/or density of the basic elements, and in which certain types of interaction are predominant.

The atoms or molecules exert forces on one another which fall off as the distance between them increases. Another factor plays a crucial role in systems made up of small elements, namely thermal agitation, which increases with the temperature of the system. Each element is continually subjected to this phenomenon, which tends to impart random motions to it in all directions. When this agitation dominates over the interaction forces, which for their part tend to bring the elements closer together, the elements will disperse as far as possible throughout the available volume, occasionally colliding with one another. This is the *gaseous state*. In this situation, the mechanical properties of the material will be associated primarily with these collisions. The force required to compress it or cause it to flow will depend on what is required to modify the number or strength of these collisions. Using statistical tools, we can then obtain exact relations between the viscosity and physical characteristics of the gas (see Sect. 2.2).

When the attractive forces are of the same order as thermal agitation, the elements tend to clump together into a compact cluster. This is the *liquid state*. In this situation, owing to thermal agitation, even though the elements remain close together, they can nevertheless move relative to one another, provided that enough of their nearest neighbours also change position, rather as happens in the celebrated Fifteen Puzzle. This means that the structure of a liquid, like the structure of a gas, is not frozen in, so to speak, but nevertheless remains statistically identical. However, we still have only a limited understanding of the relationship between the internal forces and the evolution of this disordered structure under flow conditions. So even for this simple material, we reach the limits of present day rheophysics, which, except in certain special cases, has great difficulty explaining the behaviour of condensed matter under flow conditions (see Sect. 2.3). We shall come up against this problem again when we discuss the liquid regime of other, in principle more complex, disordered materials, such as colloidal suspensions, foams, and emulsions.

In certain cases, e.g., at lower temperature or higher pressure, the material may become slightly more compact than in the liquid state and organised itself into an ordered structure, the solid state. At this point, internal interaction forces dominate over thermal agitation, which is no longer able to induce relative motions among the elements of the structure. The latter is now effectively frozen in. However, the material can still be deformed to some extent, and a direct relation can be established between the force required to do this and the local interaction forces (see Sect. 2.4). From the rheophysical standpoint, much information is provided by this situation. In a similar way, we shall be able to understand the rheophysical behaviour of various condensed systems such as foams, emulsions, and colloids in their solid state. Although these do not have a crystal structure, they do form a 'jammed' structure, from which the constitutive elements are unable to escape under the action of thermal agitation alone.

Finally, there is an intermediate state between the solid and liquid states, known as the glassy state. Here the structure is disordered as in a liquid, but thermal agitation is not sufficient to allow spontaneous motion, as in a solid (see Sect. 2.4).

2.2 Interactions Between Elementary Components and States of Simple Matter

2.2.1 Elementary Components

All matter is made up of some ensemble of atoms. To each chemical species there corresponds an atomic species. An atom comprises a nucleus and a certain number of electrons which move around this nucleus. Given the very strong forces needed to remove one of these electrons, we shall assume that, in all the physical transformations dealt with here, the atom is effectively indestructible. Atoms are usually associated together in groups known as molecules. In a molecule, the atoms are bound together by so-called valence forces which arise when they effectively share the electrons of their outermost electron shells. These forces are also strong enough to ensure that a molecule will not be destroyed during ordinary physical transformations. The electron clouds of two atoms or two molecules cannot penetrate one another because a very strong repulsive force builds up whenever such clouds come within range. We may therefore treat an atom or a small molecule of a given chemical species as an entity with a definite undeformable volume, assumed spherical for simplicity, whenever it is isolated. In the following, we shall use 'molecule' as a generic term when the relevant physical phenomena are independent of the internal structure of the elements (atoms or molecules). These molecules interact in various ways depending on the separation between them, and the mutual interaction forces may differ qualitatively.

2.2.2 Thermal Agitation

When a molecule is far removed from the other molecules in the system, it will not feel any force from them. Its motion in the vacuum is then governed by Newton's second law which, when there are no external forces (we neglect gravity here), implies that it will move with constant velocity. But for the molecule to have acquired this velocity, there must have been an impulse of some kind at an earlier time, imparting a certain energy to it. This is the energy of *thermal agitation*. If we consider systems made up of many molecules, we observe that these molecules all have different speeds and directions, i.e., they all have different velocities. The magnitudes of these velocities will be denoted here by c.

In order to quantify this agitation, we consider the average kinetic energy of the molecules. For simple systems (pure ideal gases), this has the form

$$\frac{1}{2}m\langle c^2\rangle = \frac{3k_BT}{2},\tag{2.1}$$

where T is called the temperature and $k_B = 1.38 \times 10^{-23}$ J K^{-1} is Boltzmann's constant. In this expression, the mass m of a molecule is assumed constant for all molecules in the system.

Equation (2.1) shows that the temperature provides a quantitative measure of the agitation of the molecules in a system where they are widely separated from one another. In fact, this idea is quite general. For any system, whatever the arrangement and proximity of the molecules, the quantity k_BT can be used to estimate the internal energy of thermal agitation of the elementary components. This is equal to about 0.6×10^{-20} J at typical temperatures. Thermal agitation tends to disperse a system. The internal interactions must be stronger than thermal agitation, therefore, in order to keep the molecules close to one another, as happens in a liquid or solid.

### 2.2.3 Interaction Potential

To describe the interaction forces between arbitrary objects such as molecules, it is convenient to phrase things in terms of energy. Indeed, a specific energy function can be defined for each force in such a way the force can then be derived from it. Consider a system comprising two otherwise isolated interacting bodies, i.e., exerting a force F on one another which depends on the distance x between them and which is of course zero when the two bodies are infinitely far apart (see Fig. 2.1). When there are no other forces, external to the two-body system, we can define the *interaction potential energy* Φ of the system as the energy required to bring the two bodies from infinity to a separation x. In the rest frame of the body at the origin, the idea is to bring the other body toward it from infinity to the position x. Throughout this operation, we must apply a force $-F(\xi)$, where ξ is the distance between the two bodies. The required energy is then the work done during this transfer, viz.,

$$\Phi = -\int_{\infty}^{x} F \, d\xi \ .$$

Differentiating this expression, we obtain

$$F = -\frac{d\Phi}{dx} \ .\tag{2.2}$$

Fig. 2.1 Interaction force F and interaction potential $\Phi(x)$ defined as the energy required to bring the particles from infinity to a given distance x from one another
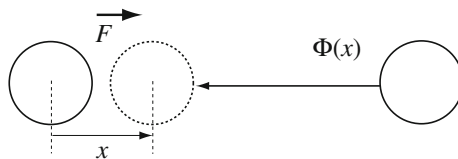
2.2.4 Van der Waals Forces

Whatever the type and structure of the molecules and their constituent atoms, there is always a short range attractive force between two molecules. This force arises because, even though the electrons are distributed uniformly on average within an atom or molecule, their instantaneous distribution will always be asymmetrical. It follows that the particle will behave as an instantaneous electric dipole, and this dipole will induce an electric field in the neighbouring atom which will in turn acquire a dipole moment, whereupon the two dipoles will attract one another.

We can use the following highly simplified argument to get some idea of the form of this interaction. Consider an atom in which the charge distribution constitutes a dipole with moment p, which is the sum of the products of the charges with their distances from a reference point located at the centre of the charges. At a distance r which is large compared with the size of the dipole, it will induce an electrostatic field E going as r^{-3}. Another dipole lying at this distance will then be polarised, that is, it will acquire a dipole of moment $p' = \alpha E$. The potential energy of interaction between these two dipoles can be written $\Phi = p'E$, which is in this case αE^2. Finally, we find that Φ is proportional to r^{-6}.

This expression is no longer valid when the molecules are too far apart (more than about ten nanometres), because the time taken by the electric field to act on the other particle is then of the same order as the typical time taken by fluctuations to vary the dipole in the first particle. This retardation effect implies that the potential goes rather as r^{-7}.

For atoms or molecules 'in contact', the interaction energy associated with these van der Waals forces corresponds to separations r roughly equal to the molecular radius, hence typically of the order of a tenth of a nanometre. The value obtained, of the order of 10^{-20} J, is close to the thermal agitation energy at room temperature. Put another way, these attractive forces, generated by effects that one might well have neglected at first glance, can play an important role in the equilibrium and structure of the system. However, this force decreases very rapidly with distance. In fact, at a separation of the order of the size of the molecules, it is already a hundred times smaller than when the molecules are in contact. Van der Waals forces thus arise mainly to ensure cohesion between molecules in contact.

2.2.5 Chemical Bonds

Within a crystal structure, molecules give up something of their independent existence in favour of ordered arrangements and strong bonds between the atoms making them up. The atoms can then bind together by valence bonds, as within a molecule. The molecules can also bind together by ionic bonds. When two atoms exchange an electron by emptying an incomplete shell of one of the atoms to fill a different level of the other atom, they then interact like two ions of opposite sign. The interaction energy between the two ions is of Coulomb type and generally much greater than the thermal energy, whence the atoms are strongly attracted to one another. To a first approximation, the corresponding interaction potential falls off essentially as the reciprocal of the distance between the elements. The order of magnitude of the energy of a covalent bond or an ionic bond is 50×10^{-20} J, hence significantly greater than the energy of van der Waals forces or thermal agitation.

2.2.6 Born Repulsion Force

This effect accounts for the impenetrability of the electron clouds of atoms or molecules. There is no general expression describing this force. Various empirical models have been developed to describe it. Their common feature is that they all predict that the force tends to infinity more quickly than all other known forces when the distance between the two elements tends to zero. The model most widely used to represent this effect is a power law, viz., $\Phi(r) = \beta/r^m$, where m takes a value greater than 7 to yield a potential much greater than all the other possible forces within a certain range. To simplify, the *hard sphere approximation* is used in some cases. This takes the potential to be infinite below some critical separation d of the molecules, whence d can be viewed as specifying their effective diameter. When there are no attractive forces, this potential is (see Fig. 2.2a)

$$r < d \implies \Phi(r) = \infty, \qquad r > d \implies \Phi(r) = 0 . \tag{2.3}$$

2.2.7 Balance of Forces

When several types of force are at work between two molecules, the total interaction potential is the sum of the corresponding potentials. In particular, when these forces are just van der Waals forces and the Born repulsion, a model commonly used to represent the total potential simply sums these two potentials, taking $m = 12$ for the repulsive potential (see Sect. 2.2.6). We then obtain the so-called *Lennard-Jones potential* (see Fig. 2.2c):

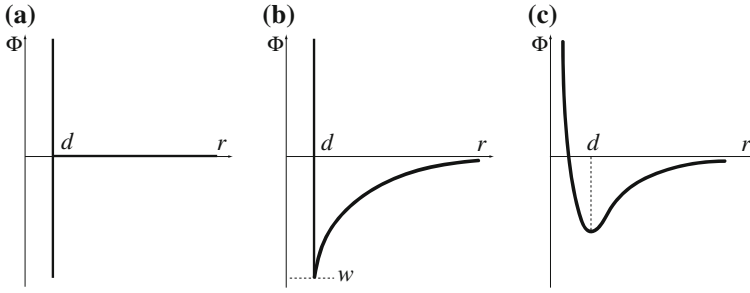$$\Phi(r) = \frac{\beta}{r^{12}} - \frac{\alpha}{r^6} . \tag{2.4}$$

Fig. 2.2 Different models for the balance of interactions between molecules. **a** Hard-sphere potential. **b** Hard-sphere potential with van der Waals attraction. **c** Lennard-Jones potential

This model can be simplified by representing the repulsive part by a hard-sphere potential within some critical distance. This is taken to be the equilibrium distance d of the molecules, associated with the minimum of the actual potential energy (see Fig. 2.2b). Hence,

$$r < d \Longrightarrow \Phi(r) = \infty, \qquad r > d \Longrightarrow \Phi(r) = -w\left(\frac{d}{r}\right)^6, \qquad (2.5)$$

where w is the maximum attractive potential, or *adhesion potential*, obtained when the molecules can be considered to be in contact, i.e., when $r = d$. The models (2.4) and (2.5) are used in particular to describe the behaviour of liquids close to the gas–liquid transition.

For solids, one can also use a more general expression for the total potential in the form of a sum of an attractive potential and a short-range repulsive potential, viz.,

$$\Phi(r) = -\frac{\alpha}{r^n} + \frac{\beta}{r^m}, \qquad (2.6)$$

where $n = 1$ and $m = 9$ for a solid with essentially ionic bonds between atoms, $n = 6$ and $m = 12$ for a van der Waals solid, and $n = 1$ and $m = 2$ for monovalent metals, i.e., with a single electron in their outer electron shell.

2.2.8 Hydrogen Bond and Hydrophobic Forces

The hydrogen bond occurs when a hydrogen atom is covalently bound to an electronegative ion such as oxygen or nitrogen. The electronegative atom will attract the electrons of the hydrogen atom very strongly towards it, thereby inducing a highly unbalanced charge distribution, to such an extent that the hydrogen atom will appear to be positively charged. Since two charges of opposite signs attract, the hydrogen

atom can then interact electrostatically with another electronegative atom. The corresponding interaction energy is of the order of 1.5–6.5 $\times$ 10^{-20} J, that is, somewhere between the energies of a van der Waals interaction and a covalent bond.

One consequence of this phenomenon is that water molecules in solution will tend to arrange themselves in such a way as to form as many hydrogen bonds as possible. For this reason, when a different molecule is immersed in water, the water molecules can react in different ways depending on the size of this molecule and its affinity with water, i.e., its ability to develop hydrogen bonds. For example, a molecule that has no particular affinity with water will cause the molecules around it to arrange themselves in such a way as to preserve as many hydrogen bonds as possible between them. This will reduce the number of possible arrangements of the molecules, and hence also the entropy of the system (see Sect. 2.4). When several elements of this type are placed in water, it is more favourable in terms of the entropy of the system for these elements to be in contact with one another, since this will reduce the area over which the water molecules must arrange themselves in some specific way. This amounts to introducing attractive forces between such elements. Interactions of this kind can destabilise a two-phase mixture by tending to make the elements of each phase gather in certain regions of the sample.

2.2.9 States of Simple Matter

Here we consider a system made up of molecules that start out far removed from one another. Such a system is in a *gaseous state*, i.e., the elements are in an excited state and only encounter one another on rare occasions (see Fig. 2.3). Disorder reigns in this state. When two molecules meet, there will be an attractive force between them, but as long as the thermal agitation remains great enough, they will not be able to hold on to one another for long. If we now reduce the temperature or the volume available to the system, the kinetic energy of the particles will decrease or collisions will become more frequent, so the particles will remain together for longer.

Below a critical temperature or volume, a condensed phase will arise, namely the *liquid state* (see Fig. 2.3). In this phase, the molecules are still agitated and the density is not yet optimal. The molecules are held very close to one another thanks to the van der Waals forces, but thermal agitation is still sufficient to maintain spontaneous relative motions of the molecules.

Below a certain temperature, the elements will organise themselves in a regular manner, in the ordered arrangement of a crystal. This generally allows the substance to obtain its optimal density. In this *solid state*, the particles are almost held motionless in their positions (see Fig. 2.3), since thermal agitation is now much weaker than the energy associated with the chemical bonds that have become established.

Finally, there is another state of matter, intermediate between liquid and solid, which can be reached by certain materials under certain conditions, in particular when we try to obtain a solid somewhat too quickly by reducing the agitation of its constituent elements without leaving them the time to order themselves into a
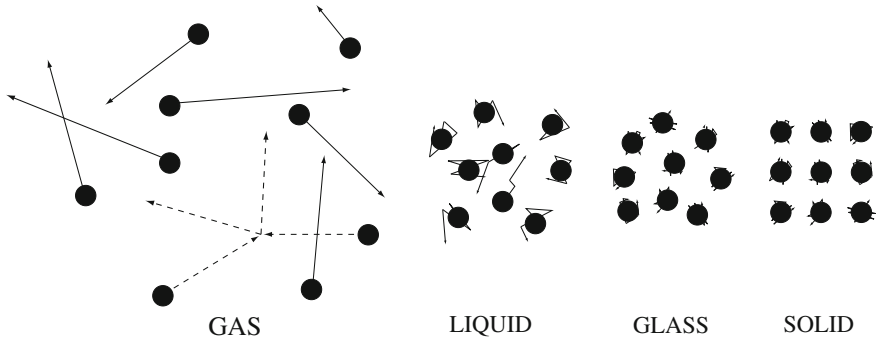
Fig. 2.3 Structure and mobility of the constituent elements in different states of matter. Molecules are represented here by *black disks* and their trajectories by *straight line segments*. The particle trajectories in the solid and glass have been exaggerated for clarity

crystalline arrangement. We then obtain an *amorphous* or *glassy state*. In this state, the resulting glass has a disordered structure similar to that of a liquid, but its constituent elements remain almost fixed in place, as in a solid.

2.3 Gaseous State

A gas is made up of widely separated molecules, in fact at separations much greater than their own dimensions. The molecules have velocities with a range of different directions and magnitudes. Each encounter between two molecules or with a solid wall gives rise to a collision. There is no other means of energy transfer within the system. The mechanical properties of the gas, that is, the way the material reacts on the macroscopic scale to the forces applied to it, are thus related to the energy exchanges through these collisions. In order to establish this relationship, it is useful to begin by characterising the state of the system in terms of the velocities and relative positions of the molecules. We will then be able to determine the mechanical properties of the material.

2.3.1 Velocity Distribution

Assuming simply that the agitation of the molecules in a given system is uniform in some statistical sense, one can establish the average characteristics of the molecular velocities without making further physical assumptions. This statistical uniformity states that the average velocities of the molecules, measured over volumes containing a large enough number of molecules or over long enough observation times, are identical in all directions and throughout the volume of the sample.

The velocity distribution is described by a probability density function $P(c)$, such that the probability of finding a velocity with magnitude between c and $c+\mathrm{d}c$ is equal to $P(c)\mathrm{d}c$. We must take into account the fact that the velocities can have different directions. The velocity vector can be represented by its three components u, v, and w in a Cartesian coordinate system. The probability of the velocity having its three components in the ranges from u to $u+\mathrm{d}u$, v to $v+\mathrm{d}v$, and $w+\mathrm{d}w$, respectively, is then $f(u)f(v)f(w)\mathrm{d}u\,\mathrm{d}v\,\mathrm{d}w$. Since the velocity distribution is independent of the direction, the function $f(u)f(v)f(w)$ will depend only on the magnitude $c = \sqrt{u^2+v^2+w^2}$ of the velocity, and we shall write it $F(c)$. Note that this is not the same as $P(c)$ because here we are only considering particular forms of velocity vectors. The direction of the velocity is independent of its magnitude and the components of the velocity are mutually independent. Therefore, changing variable and using the expression for c as a function of u, we have

$$\frac{\partial \ln F}{\partial u} = \frac{u}{c}\frac{\partial \ln F}{\partial c} \ ,$$

and noting also the relationship between F and f, which implies that

$$\frac{\partial \ln F}{\partial u} = \frac{\mathrm{d} \ln f}{\mathrm{d}u} \ ,$$

it follows that

$$\frac{1}{cF}\frac{\partial F}{\partial c} = \frac{1}{uf}\frac{\mathrm{d}f(u)}{\mathrm{d}u} \ . \tag{2.7}$$

The same can be done for the other velocity components, with analogous results. Now, since c and u can in part be varied independently, each side of (2.7) must be constant. Writing this constant in the form $-m/B$, where B is a constant, and integrating the resulting differential equation

$$\frac{\mathrm{d}f}{\mathrm{d}u} = -\frac{m}{B}uf \ ,$$

we find

$$f(u) = A\exp\left(-\frac{mu^2}{2B}\right) \ , \tag{2.8}$$

where A is a constant. If B were negative, the probability of having a velocity in a specific direction would tend to infinity when the magnitude of this velocity tends to infinity, which is not realistic. B is therefore positive. Note also that the function f is symmetric in the velocity, i.e., it does not favour any particular direction of motion. So starting from the simple assumption that this kind of agitation does not favour any particular direction, we have shown that the velocity distribution in one direction is Gaussian, centered on zero. More detailed theories of statistical physics confirm this result.

We may now calculate the probability $P(c)dc$ that the magnitude of the velocity should lie between c and $c + dc$, using the fact that this is the sum of the probabilities that the velocity vector should have magnitude c and arbitrary directions θ and φ, where the latter range from 0 to π and from 0 to 2π, respectively. We then have $du\,dv\,dw = c^2 \sin\theta\,d\theta\,d\varphi\,dc$, whence the probability distribution for the magnitude of the velocity can be written

$$P(c) = \int_{u^2+v^2+w^2=c^2} f(u)f(v)f(w)c^2 \sin\theta\,d\theta\,d\varphi\ .$$

This then implies

$$P(c) = 4\pi A^3 c^2 \exp\left(-\frac{mc^2}{2B}\right)\ .$$

The two constants A and B can be determined by using the fact that the total probability must be equal to 1, viz.,

$$\int_0^\infty P(c)dc = 1\ ,$$

together with the fact that the average value of the kinetic energy is given as a function of temperature by (2.1), viz.,

$$\langle c^2 \rangle = \int_0^\infty c^2 P(c)dc = \frac{3k_B T}{m}\ .$$

After several integrations by parts and using the standard result

$$\int_0^\infty e^{-x^2}dx = \frac{\sqrt{\pi}}{2}\ ,$$

we find that $B = k_B T$ and

$$A = \left(\frac{m}{2\pi k_B T}\right)^{1/2}\ .$$

Finally, the velocity distribution is given by

$$P(c) = 4\pi c^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mc^2}{2k_B T}\right)\ . \tag{2.9}$$

We can now calculate the average value of any quantity depending on the velocity, such as the kinetic energy. In particular, the average value of the magnitude of the velocity is

$$\langle c \rangle = \int\limits_{0}^{\infty} cP(c)\mathrm{d}c = 2\sqrt{\frac{k_{\mathrm{B}}T}{m}} \ . \tag{2.10}$$

2.3.2 Mean Free Path

The molecules of a gas are moving around all the time, so even though they are widely separated from one another, they occasionally end up in collisions. In fact, these collisions are needed to maintain the state of statistical equilibrium which ensures uniformity of the velocity distribution. This agitation effectively determines the transport properties of the gas (viscosity, diffusion, thermal conductivity) which are associated with energy transfer from one point of the system to another. In this context, an important quantity is the characteristic time for exchange of momentum between two molecules. This time is equal to the ratio of the distance between collisions and the speed of the molecules. Since we already know the velocity distribution and the average velocity (2.10), it remains only to identify the typical distance between two successive collisions of a given molecule, referred to as the *mean free path*.

For a collision to occur, the molecules must have a nonzero effective diameter d. Then any other molecule on its path with centre a distance less than d from the centre of the first in the direction perpendicular to the motion will enter into collision with it (see Fig. 2.4). Let us follow the path of a molecule, assuming that the others are not moving on average. When this molecule has travelled a distance L, it will have swept out a volume $L\pi d^2$. If n is the number of molecules per unit volume, the number of encounters with other molecules is thus $nL\pi d^2$. The average distance between two collisions is the distance allowing a single encounter, viz.,

$$\lambda = \frac{1}{n\pi d^2} \ . \tag{2.11}$$

In fact, (2.11) does indeed give the exact value up to a multiplicative factor close to unity, but one must take into account the velocities of the other molecules and the changes in direction induced by each collision.

2.3.3 Entropy

It makes no sense to try to describe the spatial distribution of the molecules directly because, given the agitation prevailing within the system, each configuration is

Fig. 2.4 Estimating the mean free path. This is the average distance travelled by a molecule (*black*) before entering into a collision with another molecule (*grey*) in a given direction
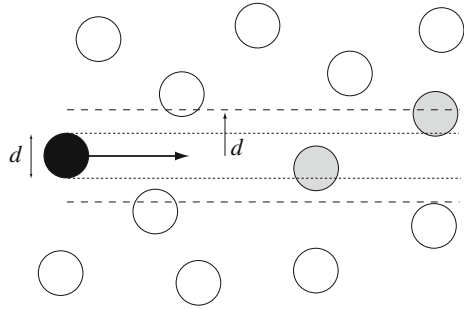
equiprobable. However, the number of degrees of freedom in positioning the elements within the available volume can be used to distinguish one system from another. To describe this idea precisely, we calculate the number Z of microscopic states that can occupy the system when it is in a given macroscopic state. We then define the *entropy*, a function of this number of microscopic states with the form $S = k_B \ln Z$. As shown in Appendix B, the entropy is related to the free energy of the system. This will prove particularly useful when describing the evolution of molecular systems or more complex systems.

In the case of an ideal gas, assuming that the internal states of the molecules are constant, we can calculate the entropy by counting up the various microscopic states specified by the positions and velocities of the molecules in the available space. We begin by counting the number of possible spatial configurations for the molecules of a gas comprising N molecules in a volume Ω. In an arbitrary volume, the centre of each molecule can of course sit at infinitely many different points. To simplify the calculation, we first assume that the centres of the molecules can only sit at a finite number of positions in a space divided up into the same number of small elementary volumes ν associated for example with the typical volume of a molecule. Note that, to obtain a better estimate of the real situation, we could choose these volumes to be much smaller. Neglecting the volume occupied by the other molecules in comparison with the volume available, which amounts to assuming that $N\nu \ll \Omega$, there are to a first approximation Ω/ν ways of placing each molecule in the given volume. The number of possible spatial configurations for the N molecules is thus $(\Omega/\nu)^N$. For identical (in fact, indistinguishable) molecules, one cannot distinguish two states that differ only by a permutation of the molecules. This means that one must divide the above number by the number $N!$ of permutations of these molecules. The number of distinct spatial configurations is therefore $(\Omega/\nu)^N/N!$.

The number of possible configurations for the velocities of the molecules could be calculated from the velocity distribution. Since the characteristics of this distribution are related to the thermal agitation, it will suffice here to note that this number is a function f of the energy U of the system and the number of molecules. We then obtain

$$S = k_B \ln \frac{f(U, N)(\Omega/\nu)^N}{N!} \ .$$

This expression can be simplified using Stirling's formula for $\ln N!$, which gives $\ln N! \approx N \ln N$ to first order. Finally, we arrive at the expression

$$S = k_{\mathrm{B}} \left[N \ln \frac{\Omega}{N} + \ln f(U, N) + C \right] , \qquad (2.12)$$

where $C = -N \ln \nu$. In (2.12), the parameter ν thus only induces changes in the additive constant C. For a given system, the number N is fixed and we are concerned with the relative changes in the variables S, Ω, and U of the system. These changes do not depend on the initial choice of volume ν.

2.3.4 Ideal Gas Law

2.3.4.1 Volume and Pressure

Consider a sample of gas placed in a solid box and hermetically sealed, except that one of its faces is in fact a movable piston. The most natural variable to characterise the constitutive material of this sample is its volume Ω, which is simply the volume within the box here because, given the thermal agitation of the molecules, it is natural to expect the gas to spread over the whole of this space. If we now inject more gas into this box, either the piston moves, thereby allowing the volume of the box to increase, or else the piston is held in place, in which case the force F required along the piston axis in order to keep it in its initial position is found to increase during the injection. There is therefore a relationship between the force and the volume of gas.

We also note that, in such a system, if we manage to increase the surface area of the piston in contact with the gas while keeping the volume of gas constant, the force increases in proportion to this area. It is thus natural to define a new variable, the *pressure* $p = F/A$, which does not depend on the area A of the surface in contact with the gas and thus characterises the state of the system.

For such a system, if each face of the box were made in the same way from a movable piston, the same pressure would have to be applied on each of these faces. In fact, this same pressure applies to each face of the box, and this would also be true for a box with polyhedral shape of any kind at all. This implies that, whatever surface element we may consider within the gas, the box could be deformed in such a way that one of its faces corresponds to this element and we would recover the same value of the pressure. For this reason, we may define the pressure at any point of the gas, and this pressure will be uniform throughout the gas. Then given this pressure, we can at last write down the force exerted by the gas on a virtual surface element of area ΔA located inside the gas. This force is equal to $-p\Delta A\,\mathbf{n}$, where $\mathbf{n}$ is the unit vector normal to the surface element (see Fig. 2.5).

Fig. 2.5 Forces induced by
the change in volume of a gas
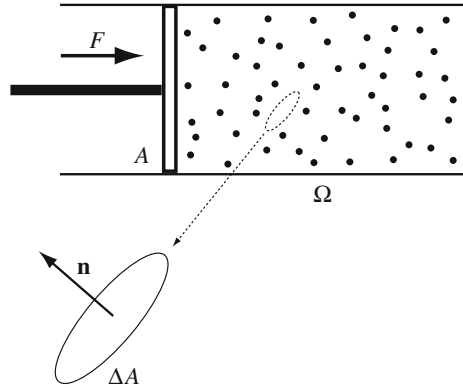
2.3.4.2 Temperature

Another physical characteristic of such a system is its temperature T. In practice, this variable can be assessed directly by our senses. If we compare two systems, we are able to say whether one is at a higher temperature than the other. The remarkable property of a gas is that, no matter how we manipulate the box discussed a moment ago, the product of the pressure and the volume is proportional solely to the number N of gas molecules in the system, provided that the temperature of the system remains the same. If we just define the temperature to be proportional to some measure of this product, we arrive at

$$p\Omega = Nk_{\mathrm{B}}T \ . \tag{2.13}$$

This is an equation of state of the material since it expresses a general relation between the fundamental physical variables associated with the material. It is also a first step toward rheophysics since it expresses the pressure (which describes the essential forces within the system) in terms of the physical characteristics of the system, and in particular the temperature. In the following, we shall see that it is effectively possible to quantify these different phenomena in terms of the physical properties of the matter on the microscopic scale. In particular, this will allow us to establish the consistency of this macroscopic approach and the microscopic description of temperature using (2.1). Note also the consistency of the equation of state of an ideal gas and the thermodynamic approach. Indeed, using (B.14), which tells us that

$$\frac{p}{T} = \left.\frac{\partial S}{\partial \Omega}\right|_{U} \ ,$$

and inserting the expression (2.12) for the entropy, we obtain (2.13) directly.
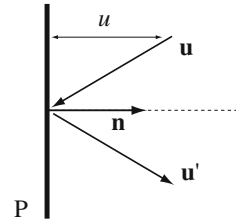
2.3.5 Kinetic Theory

To establish the relationship between the forces exerted on the gas and the macro-
scopic motions of this gas, we must pay more careful attention to the interactions
between the molecules and between the molecules and a solid surface. To tackle this
problem, we make the key assumption that these interactions are all elastic collisions.
In other words, we assume that, when one molecule encounters another, or when it
encounters a solid surface, there is no clustering effect resulting from short-range
interactions. In addition, the elastic nature of these collisions implies that energy
dissipation is negligible. These collisions can then be characterised by conservation
of momentum, and also by the conservation of kinetic energy in the system.

2.3.5.1 Pressure on a Solid Surface

Consider a particle arriving with velocity **u** at a solid wall P with total area A. This
velocity will have a normal component u along the unit normal **n** to the wall and
a tangential component which can be decomposed into two components v and w
relative to two perpendicular axes. In an elastic collision, since the wall does not
move, the particle will bounce off with a velocity **u**$'$ that has the same tangential
components v and w but normal component $-u$ (see Fig. 2.6). The particles colliding
with the wall over a time lapse Δt will be located in a layer of thickness $\Delta x = u\Delta t$
above the wall. If there are $n_{\mathbf{u}}$ particles per unit volume with velocity between **u** and
u $+$ d**u**, there will be $n_{\mathbf{u}}A\Delta x$ particles in this layer during the time Δt, and there will
therefore be $n_{\mathbf{u}}Au$ collisions per unit time.

By Newton's second law, the resulting force on the wall is equal to the total
momentum imparted to the wall per unit time, i.e., $f(t) = m\mathrm{d}v/\mathrm{d}t$. For a collision
like the one described above, the molecule has a constant velocity **u** up to the time
when it hits the wall. Its velocity will then change quickly to a new value **u**$'$. As
a function of time, the force associated with this collision is thus sharply peaked
about the moment of contact. Before contact, the force is zero, then at the beginning
of contact, the speed is reduced, inducing a positive force up until the time when
the molecule comes to a halt (zero speed). The force reaches its maximum value at
this time. Subsequently, the motion is reversed and the force will drop off more or
less symmetrically. As a result of this collision, the average force on the wall in the

normal direction $\mathbf{n}$, between two times before and after the collision separated by a time lapse Δt, is thus

$$\langle f \rangle = \frac{1}{\Delta t} \int\limits_0^{\Delta t} f \, dt = \frac{1}{\Delta t} \int\limits_0^{\Delta t} m \, dv = \frac{2mu}{\Delta t} \, . \tag{2.14}$$

The wall is struck many times by particles with the same velocity and the total average force is thus the sum of the average forces (2.14) associated with each collision, viz., $F = n_{\mathbf{u}} A u \Delta t \langle f \rangle$. Typical pressure measurements are made over areas and time lapses such that the number of impacts taken into account is extremely high. For this reason, one would never notice the fluctuations due to the succession of collisions at different speeds, and the effective force measured is very close to the total average force calculated above. Finally, the pressure exerted by all the collisions taken together is given by

$$p = \frac{F}{A} = 2n_{\mathbf{u}} m u^2 \, . \tag{2.15}$$

We now calculate the kinetic energy of a molecule. We have $c^2 = u^2 + v^2 + w^2$ and denote the number of particles per unit volume with speed c by n_c. This set of particles comprises subsets with different values of the velocity component u. However, the square of each velocity component will have the same average over all the molecules with speed c, because no direction is favoured. Each will thus be equal to $1/3$ of c^2, whereupon we obtain

$$\frac{1}{n_c} \sum_{\mathbf{u}} n_{\mathbf{u}} u^2 = \frac{c^2}{3} \, .$$

We can now calculate the pressure exerted on a wall by all the molecules with speed c. In this ensemble, only those molecules with velocity directed toward the wall will actually collide with it. This corresponds to half of the ensemble. The total pressure exerted by the particles with speed c is thus given by

$$p = \frac{1}{2} \left(2m \sum_{\mathbf{u}} n_{\mathbf{u}} u^2 \right) = \frac{1}{3} m n_c c^2 \, . \tag{2.16}$$
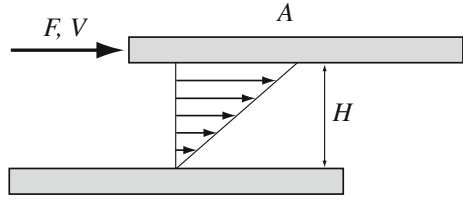
Since by definition

$$\langle c^2 \rangle = \frac{1}{n} \sum_c n_c c^2 \, ,$$

the total pressure due to the impacts of all the particles is given by

$$p = \frac{1}{3} m n \langle c^2 \rangle \, .$$

Fig. 2.7 Simple shear. The
material is sheared between
the two solid surfaces (*grey*).
The fluid layers slide one over
the other, parallel to these
surfaces

For a volume Ω containing a total of N particles, we have $n = N/\Omega$ and the above
equation becomes

$$p\Omega = \frac{1}{3}mN\langle c^2\rangle \ . \tag{2.17}$$

Using the expression for the average kinetic energy of a molecule due to thermal
agitation as given by (2.1), we note that (2.17) is nothing other than the equation of
state (2.13) of an ideal gas. We have thus found a direct relation between the pressure
in a gas and the kinetics of its constituent molecules.

2.3.5.2 Viscosity

In the above discussion, the gas as a whole was at rest, i.e., any motions occurring
within it did so without changing the shape of its apparent volume. We now consider
what happens when certain regions of the gas are in motion relative to others. In this
context, the simplest situation is when one plane layer of gas moves in a direction
lying within this plane and relative to two adjacent layers. To maintain such a relative
motion at some speed v between two layers, it turns out that one must exert a tangential
force F in the direction of motion, and this whatever material we may consider. If
we imagine the system divided into a large number of identical layers of thickness
Δy and apply a force F on the upper layer, this force will also apply to all the layers,
displacing each at a speed Δu relative to the layer just beneath it. This kind of motion
is called a *simple shear* (see Fig. 2.7).

In this kind of flow, the relative speed between the two solid surfaces separated
by a distance H can be expressed as the sum of the relative speeds of the $H/\Delta y$ pairs
of adjacent layers, whence

$$V = \frac{H}{\Delta y}\Delta u \ .$$

Repeating with a series of layers with another thickness $\Delta y'$, we would obtain the
same result. The ratio $\Delta u/\Delta y$ of the relative speed of the layers and their thickness
is thus constant and equal to V/H. This quantity is called the *shear rate* and we write

$$\dot{\gamma} = \frac{\mathrm{d}u}{\mathrm{d}y} \ . \tag{2.18}$$

The ratio between the tangential force and the area of the layers is the *tangential* or *shear stress* $\tau = F/A$. It has physical dimensions of pressure and is thus given in pascals (Pa). One would expect this variable, which expresses the resistance to friction between the sliding layers, to depend on the relative speed of the layers, and hence on the shear rate. We can thus define the *apparent viscosity* of the material by

$$\eta = \frac{\tau}{\dot{\gamma}} \; . \tag{2.19}$$

In practice, this type of flow can be obtained by putting the fluid between two parallel solid walls and imposing a relative parallel motion of these two walls (see Fig. 2.7). The gas layers close to the walls will tend to move a the same speed as the walls, and this induces a relative motion of the different layers. The tangential force applied to the walls is transmitted to the other layers of the material and, in the stationary regime, one expects a uniform simple shear.

It may seem strange to have to exert a force in order to shear a gas. In fact, this can be understood using the following picture. Two neighbouring gas layers behave like two trains travelling in the same direction but at different speeds $V_1 < V_2$, each train being full of excited travellers (the molecules) running in all directions inside their train (due to thermal agitation) and occasionally jumping from one train to the other. Even if each train always carries the same number of travellers, some travellers will arrive in the faster train with speed V_1 and others will arrive in the slower train with speed V_2. Under these conditions, the faster train will tend to slow down unless it is supplied with some extra energy, and the slower train will tend to accelerate unless some energy is removed from it. This is why a tangential force has to be applied between the two fluid layers to hold their relative speed constant.

With the help of this mechanism, we may now calculate the viscosity of a gas using the kinetic theory developed earlier. A detailed calculation would involve a rather sophisticated formalism, but we shall simplify here. We represent the gas in simple shear flow by plane layers sliding one over the other, each layer exchanging energy with its neighbours, like the two trains in our analogy. The thickness of these layers is of the order of the mean free path, since a distance of this order is required by each molecule to exchange energy with another molecule. We assume that, as soon as one molecule arrives in the neighbouring layer, it imparts its momentum to this layer through a collision, thus neglecting the possibility of the molecule actually crossing the layer without collision. Furthermore, we assume that the velocity distribution is the equilibrium distribution we determined earlier, in other words, that the momentum exchanges are instantaneous.

Consider two layers of gas of thickness λ (the mean free path) in relative motion (see Fig. 2.8). Viewed from a frame moving with the lower layer, the latter is of course fixed while the upper layer moves at a speed $V = \dot{\gamma}\lambda$. Each layer 'ejects' and 'absorbs' molecules all the time at a rate q which is just the number of molecules crossing the interface per unit time. A molecule coming from the lower layer and entering the upper one has a speed equal to its agitation speed within gas that is macroscopically at rest, while each molecule leaving the upper layer and entering

Fig. 2.8 Momentum
exchanges due to molecules
moving from one layer to the
next during simple shear
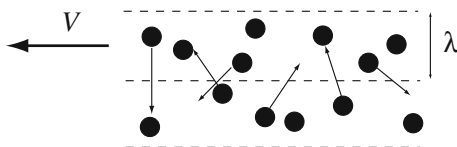
the lower one has this agitation speed plus the speed V of the layer as a whole. The
change in the momentum of the upper layer per unit time in the direction of relative
motion of the layers is thus $-qmV$. By a similar calculation to the one we did for
the pressure, it follows that the force exerted by the lower level on the upper level
is $-qmV$. We deduce that the shear stress that must be applied to the upper layer to
maintain this motion is $\tau = qmV/A$.

We now calculate the flow q of molecules through a surface per unit time. Accord-
ing to the discussion in previous sections, we know that $n_{\mathbf{u}}Au$ particles of speed u
cross the area A per unit time. The total number of molecules crossing A per unit
time is thus obtained by summing over all possible magnitudes of the velocity, which
yields $nA\langle u\rangle_+$, where

$$\langle u\rangle_+ = \frac{1}{n}\sum_{u>0} n_{\mathbf{u}}u \ .$$

The quantity $\langle u\rangle_+$ can be determined directly from the velocity distribution (see
Sect. 2.3.1), and in particular using (2.8), with the result

$$\langle u\rangle_+ = \int_0^\infty uf(u)\,\mathrm{d}u = \frac{1}{4}\langle c\rangle \ . \tag{2.20}$$

It follows that $q = nA\langle c\rangle/4$. Finally, the apparent viscosity $\tau\dot{\gamma} = qmV/A\dot{\gamma}$ of the
gas is given by

$$\mu = \alpha mn\lambda\langle c\rangle = \frac{2\alpha}{\pi d^2}\sqrt{mk_{\mathrm{B}}T} \ , \tag{2.21}$$

where α is a coefficient equal to 1/4 according to this simplified calculation. If we take
into account the more complex reality of momentum exchanges within the gas, we
find $\alpha = 1/2$. At room temperature, the order of magnitude of the viscosity of a gas is
10^{-5} Pa s. According to (2.21), we note that the viscosity of an ideal gas increases with
the temperature. This is quite the opposite of what is generally observed for liquids
(see Sect. 2.4.5). It arises because the internal friction mechanisms are directly related
to thermal agitation, which of course increases with temperature. Another remarkable
property is that, to a first approximation, according to (2.21), the viscosity of the gas
does not depend on its density, something which confirms that the physical origin of
viscous friction is essentially the agitation energy of the molecules, however many

of them there are. A final important point is that the viscosity coefficient obtained above does not depend on the shear rate $\dot{\gamma}$. The ideal gas is a *Newtonian fluid*.[1]

2.3.5.3 Viscous Dissipation

It is useful to calculate the energy that must be supplied to maintain the relative motion under simple shear as described above. Given that the motion is maintained, we can calculate the energy per unit time, that is, the power that must be supplied to the system. The power required to displace two neighbouring layers relative to one another is the product of the applied force and the relative velocity, viz., $\tau A \dot{\gamma} \lambda$. The total power needed to shear a volume of gas of thickness H is thus the sum $\tau A \dot{\gamma} \lambda$ over all the layers of thickness λ, namely, $\tau A \dot{\gamma} H$, or again,

$$P = \tau \dot{\gamma} \Omega, \tag{2.22}$$

where $\Omega = AH$ is the volume of the sample under shear.

The power supplied here is often considered to be dissipated power and referred to as *viscous dissipation*. In practice, the corresponding energy must effectively be supplied continuously to maintain the motion despite the friction between the layers as they slide over one another. According to the first law of thermodynamics, this energy contributes to increasing the internal energy of the system, and hence eventually to increasing the temperature of the gas. On the other hand, heat exchange with the surroundings, and in particular with the solid walls, may allow the system to remain at the same temperature. In any case, these effects are usually negligible for gases because the shear rates encountered in practice are actually very low compared with the kinds of speeds attained by molecules within the gas at macroscopic rest, and which characterise the internal energy of the material. However, these effects may nevertheless become significant for viscous liquids under high shear rates.

2.4 Liquid State

2.4.1 Transition from Gaseous State to Liquid State

2.4.1.1 Possible Existence of a Condensed State

When describing the gaseous state using the kinetic theory for ideal gases, which was consistent with the equation of state (2.13), we assumed that the molecules could not congregate together and that they remained on average rather far from one another.

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[1] In this book, we shall use μ for the viscosity when discussing Newtonian fluids, and η for the apparent viscosity when the latter is not necessarily constant.

If volume effects or interaction forces play a significant role, this is no longer justified. The probability of collisions between molecules increases with their density, and when the molecules of a gas encounter one another, there is a certain probability that they will stick together. This probability goes up as the temperature drops, since the kinetic energy of the molecules then decreases. To get a better understanding of this phenomenon, it is instructive to consider the changes in the energy of a system when the molecules are brought closer together.

Consider a material made up of non-polar molecules, that is, molecules such as oils (hydrocarbons or silicones) with no net electric charge and no permanent dipole moment. Under these conditions, the only forces between molecules are the van der Waals attraction and repulsive forces. In order to describe the corresponding mutual interaction potential, we shall use the modified hard-sphere potential defined by (2.5).

We now calculate the total interaction potential energy Φ_T of a molecule with all the other molecules of the system. To do this, we must sum the potentials, but taking into account the spatial distribution of the surrounding particles. However, we know that the mutual interaction potential drops off very quickly with the relative distance between molecules. To a first approximation, we may therefore simply take into account the molecules in the immediate neighbourhood of the chosen molecule, that is, at a centre-to-centre distance equal to their size d. Treating the molecules as spherical, there will be on average $4\pi d^3 n/3$ molecules in contact with the given molecule, whence the total potential can be written

$$\Phi_T = -\frac{4}{3}\pi d^3 n w \ .$$

Adding up all the potentials calculated in this way over the whole ensemble of molecules, we would obtain a total potential with a double count of the potential associated with each mutual interaction. The average potential per molecule is thus given by $\Phi_T/2$, which we write more simply using $\alpha = 2\pi d^3 w/3$ and $\Omega_m = 1/n$, the average volume available per molecule:

$$\Phi = -\frac{\alpha}{\Omega_m} \ . \tag{2.23}$$

If the molecules are stacked up on top of each other as in a compact disordered pile of grains (see Sect. 3.2), the volume fraction ϕ, i.e., the ratio of the volume of the molecules to the total volume, is of the order of 64 %. The volume available per molecule is therefore the volume of one molecule divided by 0.64, or $\Omega_m = \pi d^3/6 \times 0.64$. The energy per molecule is then of the order of $6w$, or a few times $k_B T$. In this situation, the total attractive potential of a molecule with its neighbours is distinctly greater than its energy of thermal agitation. The latter will not therefore be sufficient for it to break away easily from its set of neighbours. This shows that a stable *condensed state*, in which all the molecules are very close to one another, is quite feasible. We shall now investigate the conditions under which the transition to such a

state becomes possible. To do this, we shall examine the evolution of the free energy of the system, which depends in particular on the entropy (see Appendix B).

2.4.1.2 Entropy of the System

Since we are now considering the possibility of condensed states, we may no longer assume as we did when calculating the entropy of a gas (see Sect. 2.3.3) that the volume of the molecules is negligible compared with the volume of the system. We must now take into account the reduction of accessible volume within the system that results simply from the presence of the other molecules. We shall further assume that the second term on the right-hand side of (2.12), relating to the velocity configurations, is not for its part significantly affected by the increase in the density of molecules or their interactions. (A more detailed investigation does in fact demonstrate the general validity of this assumption.)

Imagine once again that the molecules are placed successively within the volume Ω. The number of possible positions for the first molecule is still equal to the number of volume elements, viz., Ω/v. Now that this molecule occupies one of the volume elements, the volume available for the second molecule is $\Omega - v$. However, one must also take into account the so-called excluded volume around a molecule, due to the fact that two molecules cannot come closer than a certain centre-to-centre distance equal to their diameter. For a spherical molecule of volume v, it is straightforward to show that the total excluded volume when positioning the centre of another molecule is $8v$. For the second molecule, the number of possible positions is therefore only $(\Omega - 8v)/v$. Under these conditions, if we continue to add molecules in this way, for the k th molecule, there will remain only

$$\frac{\Omega - 8\beta_k(k-1)v}{v}$$

possible positions. In this expression, β_k accounts for the fact that the excluded volumes calculated in each step may overlap and hence have less impact on the reduction of the available volume. This factor will be equal to 1 for the first few molecules, but will then fall off as the number of added molecules increases.

Taking into account the possible permutations of the N molecules in a given configuration, it follows that the number of configurations is

$$Z \propto \frac{1}{N!} \prod_{k=1}^{N} \frac{\Omega - 8\beta_k(k-1)v}{v} \, .$$

To estimate this product, we take a kind of average value of the factors, given that they vary between Ω and $\Omega - 8\beta_N(N-1)v$. Hence, to a first approximation, we assume that the above expression can be rewritten in the form

$$Z \propto \frac{1}{N!} \left(\frac{\Omega}{\nu} - \beta N \right)^N , \qquad (2.24)$$

introducing a kind of 'average' factor β. Using the available volume per molecule Ω_m/N, the entropy per molecule $S_m = S/N$ becomes, up to a constant,

$$S_m = k_B \ln(\Omega_m - \beta \nu) . \qquad (2.25)$$

2.4.1.3 Equation of State

In order to find the equation of state of the system, we cannot consider entropy changes alone, because the changes in available volume now have an impact on the internal energy. We must in fact calculate the Helmholtz free energy (see Appendix B). The total internal energy U of the system is the sum of the kinetic energies of the elements making up the system, i.e., $3k_B T/2$ per molecule, and the internal potential energy given by (2.23). The second term in the free energy can be deduced from the expression (2.25) obtained for the energy, whence the average free energy per molecule is

$$\mathscr{F}_m = \frac{3}{2} k_B T - \frac{\alpha}{\Omega_m} - k_B T \ln(\Omega_m - \beta \nu) . \qquad (2.26)$$

By (B.15), viz.,

$$p = - \left. \frac{\partial \mathscr{F}}{\partial \Omega} \right|_T = - \left. \frac{\partial \mathscr{F}_m}{\partial \Omega_m} \right|_T ,$$

we then obtain

$$p = - \frac{\alpha}{\Omega_m^2} + \frac{k_B T}{\Omega_m - \beta \nu} . \qquad (2.27)$$

In this relation, we may insert the total volume to obtain the most usual form of the so-called *van der Waals equation of state*:

$$p = \frac{N k_B T}{\Omega - \beta N \nu} - \frac{\alpha N^2}{\Omega^2} . \qquad (2.28)$$

This provides a good qualitative description of the behaviour of an ensemble of molecules over a rather broad range of states. Let us consider some of its predictions, concerning in particular the dependence of the pressure on the volume at different temperatures. When the temperature is high enough, the second term in (2.28) becomes negligible for all values of the volume, because the volume cannot be made to tend to zero. In this case, the pressure therefore falls continuously as the volume increases (see Fig. 2.9): the system variables do not give any sign of a change of state. Note, however, that the pressure tends to infinity when the volume of the system tends to $\beta N \nu$, so there is no possible state for a smaller volume.

Fig. 2.9 Typical isotherms
$T = $ const. obtained from the
van der Waals equation (2.28).
Upper curve high temperature.
Lower curve low temperature.
These *curves* can be used to
define the liquid and gaseous
states of the material (see text)
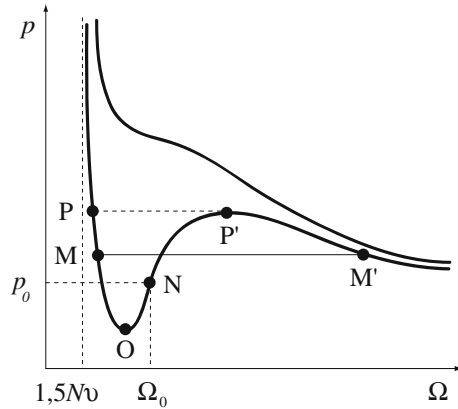
We may take it that the densest possible disordered state is reached for this value. Now we know that the maximal stacking concentration of a disordered ensemble of beads is 64 %. Here the concentration is the ratio of the effective volume $N\nu$ occupied by molecules to the available volume Ω. It thus makes sense to take $\beta = 1.5$, which leads to a divergence of the pressure for a concentration $N\nu/\Omega \approx 0.64$.

When the temperature is high enough, there is a region between the points O and P' in the example of Fig. 2.9 where the pressure grows with increasing volume. This region does not correspond to a stable state. Indeed, if there are slight fluctuations in the characteristics of the system within the sample, these will quickly degenerate, i.e., they will increase in amplitude, thereby inducing significant non-uniformities into the state of the system. For example, consider a point N with coordinates (p_0, Ω_0) in this region of the curve. If the volume available per molecule is at a given time slightly greater than Ω_0/N in part of the system, the pressure y is greater than p_0. In the rest of the system, the volume per molecule is then on average smaller than Ω_0/N and the pressure y is less than p_0. To try to reestablish pressure equilibrium in the various parts of the system, the region of higher pressure will tend to expand even further, climbing well beyond the point N on the curve, while the region of lower pressure will tend to shrink, falling well below the point N. The fact that the slightest local fluctuation in the variables is amplified in this way means that the system is unstable.

The two other regions of the lower curve in Fig. 2.9, where the pressure decreases with increasing volume, correspond to stable regimes. The stable region associated with the first part of the curve (up to the point O) is what we shall call the *liquid state* of the material. The volume available per molecule is small, of the same order as the volume of the molecule, and hardly sensitive to changes in pressure. In this regime, the term associated with interactions and the entropy term in (2.28) both play an important role in the expression for the pressure. The second stable region (beyond the point P') is associated with the *gaseous state*. The volume is well above the total volume of the molecules and varies rapidly with changes in the pressure.

In this case, the interaction term is negligible, cohesive effects are almost zero, thermal and entropic effects dominate, and the density is low.

Given the instability of the intermediate region between the two states, there is no way of going continuously from the liquid to the gaseous state. When the pressure is gradually reduced from a point in the upper part of the curve, we remain in the liquid state and the volume increases slowly. But as soon as we reach a state (for example, at the point M) below the point P associated with the maximum pressure of the unstable region, the system can go to the gaseous state (at the point M' in our example) situated at the same pressure on the other stable part of the curve. The exact point at which this phase transition occurs depends on the rate at which the pressure is reduced. If it is reduced very slowly, the transition will occur around the point P, but if it is reduced quickly, the point O can be reached before the transition occurs. Between the points P and O, the liquid is said to be *metastable*.

2.4.2 Structure

A liquid consists of a dense but disordered stack of more or less spherical molecules. At short range, that is, considering only the nearest neighbours of a molecule, there is an organisation close to what we see in a crystalline solid, for there is then only a limited number of stacking possibilities. However, at longer range, the small successive deviations from an organised structure lead eventually to a totally disordered one.

In the liquid state, the molecules are characterised on the one hand by the fact that they are in some sense 'stuck together' by the attractive van der Waals force, and on the other, by the fact that they are subject to permanent thermal agitation, which allows them to move around their neighbours and even 'unstick' themselves from time to time.

2.4.3 Deformation

Let us consider what happens when a simple shear deformation is imposed on a liquid. Suppose first that this deformation is imposed extremely quickly, in fact so quickly that thermal agitation has no time to play any role. Under such conditions, for a small deformation, a given molecule (see Fig. 2.10) will retain the same set of neighbours, while their relative distances will increase slightly. Some neighbouring molecules will come closer and others will move away. This implies that the relative distance of the molecules is no longer the distance corresponding to the potential energy minimum associated with the interaction forces (see Fig. 2.2), whence the total interaction potential energy will rise. As in the case of a solid subject to a small deformation (see Sect. 2.6), the stress required is proportional to the deformation and the system returns to its initial position as soon as the stress is released. The liquid can be considered in this regime to behave in an essentially elastic way.
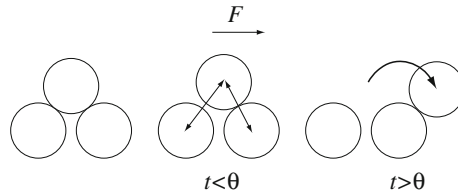
Fig. 2.10 Deformation and relaxation within a liquid subjected to a stress from time $t = 0$ (schematic view). *Left* the liquid is at rest. *Centre* the liquid deforms without rearrangement after a short time. *Right* rearrangement occurs

This regime is only observed if the above forces are applied for extremely short times. Indeed, under typical conditions, in contrast to a crystalline solid, a liquid has time to rearrange itself. Indeed, the fluctuating motions of the molecules due to thermal agitation allow them to explore a whole range of spatial configurations in a very short space of time. Such a rearrangement is able to 'relax' the internal stresses resulting from the potential energy stored up during the tiny relative displacements of the molecules. Finally, in practice, the force required to maintain a deformation falls to zero after a short time, whereupon the liquid recovers a structure equivalent to its initial structure before deformation. There is therefore a characteristic time known as the *relaxation time* θ beyond which we may consider that thermal agitation will have allowed the molecules to explore the various configurations close to their initial state. The elastic regime can only be observed over times shorter than θ. For simple liquids, we find that θ takes values between 10^{-12} and 10^{-10} s. Consequently, these materials only exhibit an apparent solid behaviour for extremely fast external intervention, behaving like simple fluids on the time scales relevant to most experimental situations. On the other hand, materials with relaxation times comparable with typical observation times will have more complex rheological properties than liquids under these same conditions. This is in fact the case for all the materials to be discussed subsequently in this book. We shall see later on that the fast relaxation of simple liquids also underlies their simple mechanical (Newtonian) behaviour, which suggests that the non-Newtonian behaviour of complex fluids results from slow relaxation phenomena.

2.4.4 Flow

When a large enough deformation is imposed, there is no other solution but to force neighbouring molecules to move apart permanently. For the moment, we assume that thermal agitation can be neglected. We shall assume that the molecules are aligned in parallel layers and remain so. We then impose a simple shear in the direction of one of these layers (see Fig. 2.11). This shear will induce a relative motion of the layers in this direction, and during this motion, some molecules will begin to come

Fig. 2.11 Modelling the flow behaviour of a liquid in the absence of thermal agitation. Relative motions of a molecule and two of its neighbours and changes in the interaction potential energy and the force required to impose this motion. Different relative positions of the molecules (**a**, **b**, **c**) (*right*) associated with different levels of interaction energy and force (*left*)
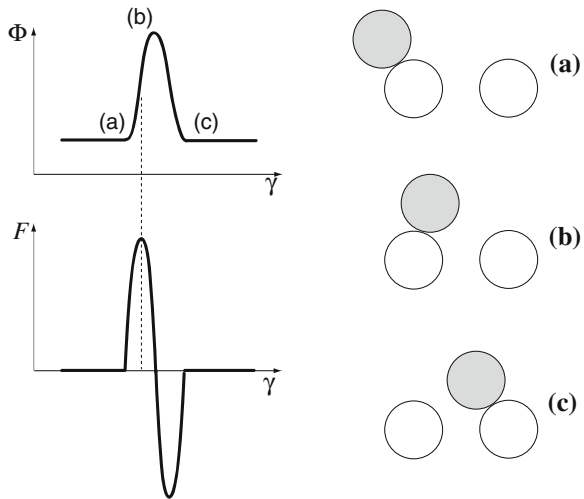
closer, while others will move apart (see Fig. 2.11). This induces an increase in the potential energy associated with short-range interactions, since the initial equilibrium position (a) probably corresponded to a minimum potential energy. Beyond a certain displacement associated with a maximum value, located at (b), the potential energy begins to decrease, then returns to zero at (c), when the system recovers an analogous configuration to the original one. We can use the gradient of the potential energy as given by (2.2) to estimate the changes required of the applied force in order to follow such a development (see Fig. 2.11). When the force required is negative, there is no need to apply any force at all, for the system will return to its original configuration of its own accord. The average force to be imposed is the integral over all positive force values. Note that, in this argument, only the interaction potential energies are relevant. The resulting average force does not therefore depend on the relative speed of the layers, i.e., the shear rate. This corresponds to a (plastic) behaviour of type $\tau = $ const. which obviously differs from the viscous behaviour we expect to find in a liquid: the higher the shear rate, the greater the force required to maintain the flow.

This comes about because we have not taken thermal agitation into account. This is what allows the molecules to rearrange themselves very quickly at each instant of time. Indeed, it is not necessary to supply all the energy associated with the separation of neighbouring molecules since their own kinetic energy can contribute significantly here. To get a better understanding of this phenomenon, we first investigate the effect of agitation on the structure of the liquid at macroscopic rest (without external forces, in a non-deformable container). Due to the high concentration of the system, each molecule is as though emprisoned in a cage formed by its neighbours. However, the position of the cage walls fluctuates as time goes by due to the agitation of the molecules around it, whence the local density can be reduced by rearranging the system slightly. In this way, from time to time, a 'hole' appears in the cage, large enough for the molecule to escape. If at this time it has enough kinetic energy to

overcome the attractive force of its neighbours, it can then completely escape from its cage. When the liquid is at macroscopic rest, such movements of one molecule in one direction or another tend to balance out.

On the other hand, when a stress is imposed on the system, it will favour motions in one particular direction by reducing the energy needed by the molecules to get out of their cage in that direction. In this situation, the flow is like a destabilisation of an equilibrium situation, favouring one specific direction. The extent of this desta-bilisation increases with the magnitude of the stress which reduces the height of the energy barrier, and it can be expressed via the relative displacement speed of the layers, that is, via the shear rate. In practice, *Newtonian behaviour* is observed for simple liquids, as for gases:

$$\tau = \nu\dot{\gamma} \ , \tag{2.29}$$

where ν is here the viscosity of the liquid.

Apart from the increase in the stress with the shear rate discussed above, (2.29) also expresses the fact that a flow at constant velocity will set up instantaneously when given stress is applied. Given what was said above, this is valid as long as the characteristic flow time, i.e., the time $1/\dot{\gamma}$ required to reach a deformation of $100\,\%$, is significantly longer than the relaxation time θ of the system. This is of course true most of the time. Another feature expressed by (2.29) is the fact that the behaviour of the material does not depend on the history of the flow. The shear rate achieved depends only on the stress applied at the given time. These properties all arise due to the very fast relaxation of the liquid which, thanks to the thermal agitation of the molecules, tends to forget almost instantaneously the deformations it has just undergone.

2.4.5 Rheophysical Model

The Eyring model is based on the qualitative principles discussed above. It assumes that, through its interactions with its neighbours, each molecule behaves at each instant of time as though it were in a potential well of average depth ε and trying at regular intervals to escape from this well with the help of thermal agitation. To do so, the molecule must have greater kinetic energy than ε. We thus seek the probability of a molecule within the system having such an energy. We may assume that the velocity distribution of the molecules is the same as in a gas. The desired probability is then

$$\int_{mc^2/2>\varepsilon} P(c)\,\mathrm{d}c \ ,$$

which, according to (2.9), is proportional to $\exp(-\varepsilon/k_\mathrm{B}T)$. The frequency with which a molecule leaves its well, i.e., the number of jumps made by a given molecule per unit time, is proportional to this probability and to the frequency C of attempted jumps:
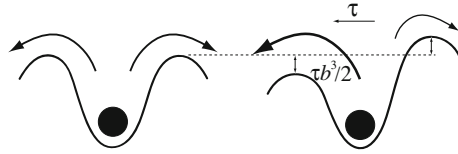
Fig. 2.12 A molecule escapes from its potential well with the help of thermal agitation. *Left* equally probable motions in all directions. *Right* asymmetrical motions resulting from modification of the potential barrier in a specific direction due to application of a stress

$$C \exp\left(-\frac{\varepsilon}{k_B T}\right) . \tag{2.30}$$

Eyring suggested taking C to be a vibration frequency approximately equal to $k_B T/\hbar$, where $\hbar = 6.63 \times 10^{-34}$ m^{2}kg s^{-1} is Planck's constant. Note that, since ε is the energy needed to get the molecule out of its liquid environment, we should expect it to correspond to the latent heat of evaporation per molecule ε' (see Sect. 2.4.6). In practice, for many liquids, the relation is rather of the form $\varepsilon \approx 0.4\varepsilon'$. Note also that (2.30) can be interpreted as the reciprocal of a characteristic time required by the system to undergo an elementary change of configuration. It is thus also the relaxation time θ of the system, beyond which the system forgets the deformations it has undergone (see Sect. 2.4.3).

When no stress is applied to the system, the probability of a molecule leaving a well is equal to the probability of a molecule turning up there, which means that the system is at rest macroscopically. Suppose now that a shear stress is applied to the system. The jumps in the direction of the force corresponding to this stress are no longer balanced out because it is easier to leave the well in the direction of the force than in the opposite direction. Let b be the average distance between the centres of two neighbouring molecules. During an elementary displacement of the typical length required to get to the top of a well, i.e., $b/2$ (see Fig. 2.12), the work done on a molecule is the product of the applied force τb^2 and the displacement, that is, $\tau b^3/2$. The energy barrier that must be overcome to accomplish such a jump is reduced by this much. On the other hand, the energy barrier in the opposite direction is increased by this same amount, whence the frequency of jumps per unit time in the direction of the applied force, which is the difference between the frequencies of jumps in the two directions, can now be written

$$f = \frac{kT}{\hbar} \exp\left(-\frac{\varepsilon}{k_B T}\right) \left[\exp\frac{\tau b^3}{2k_B T} - \exp\left(-\frac{\tau b^3}{2k_B T}\right)\right] .$$

When $\tau b^3 \ll 2k_B T$, this expression simplifies to first order, yielding

$$f \approx \frac{\tau b^3}{\hbar} \exp\left(-\frac{\varepsilon}{k_B T}\right) . \tag{2.31}$$

We now consider two parallel plane layers of molecules in relative motion at a distance b from one another, under the action of a shear stress τ in the direction of the planes. The instantaneous motions of the various molecules in each layer are not identical, but their average velocity is uniform and can be found from (2.31). Indeed, the speed of one of the layers relative to the other as induced by this motion can be written $V = bf$. We deduce that the shear rate is $V/b = f$. Finally, we obtain the apparent viscosity of the liquid in the form

$$\eta = \frac{\tau}{\dot{\gamma}} = \frac{2\hbar}{\Omega_{\mathrm{m}}} \exp \frac{\varepsilon}{kT} \, , \tag{2.32}$$

where $\Omega_{\mathrm{m}} \approx b^3$ is the volume available for each molecule. The right-hand side is independent of the shear rate so the apparent viscosity η is constant and this model effectively predicts that a simple liquid will have *Newtonian behaviour*. Note, however, that (2.32) is not necessarily valid unless the viscous energy associated with a unit deformation is much less than the thermal energy, i.e., $\tau \Omega_{\mathrm{m}} \ll 2k_{\mathrm{B}}T$. This is true in most cases for liquids made up of small molecules, i.e., with diameter of the order of a few angstroms, and at temperatures that are not too low.

Equation (2.32) agrees quite well with the observed temperature dependence of liquid viscosities. In contrast to gases, the viscosity decreases with temperature. In other words, a liquid is fluidified by increasing the thermal agitation. This is because we thereby increase the frequency with which the elements jump from one cage to another. As an example, water has viscosity 1.787×10^{-3} Pa s at $0\,°C$ and 0.295×10^{-3} Pa s at $100\,°C$, a value about a hundred times greater than for a gas. The values are of the same order of magnitude for ethyl alcohol and mercury. In contrast, glycerol has viscosity 12 Pa s at $0\,°C$ and 1.5 Pa s at $50\,°C$.

Note also that the pressure does not appear in the above expression for the viscosity. In practice, this is usually the case. The pressure has little influence on the viscosity of liquids because an increase in pressure would induce a slight reduction in the intermolecular distance and hence in the interaction energy, but it would not significantly modify the frequency of jumps determined above.

2.4.6 Interfacial Tension

Energy is required to create a liquid–gas interface. This phenomenon is due to the cohesive (van der Waals) forces between the liquid molecules. A molecule immersed in the liquid, hence surrounded solely by liquid molecules, has a total interaction potential energy (*cohesive energy*) $n_0 w$, resulting from its interactions with its n_0 nearest neighbours. In practice, it is simpler to use the cohesive energy per unit area $w_{\mathrm{L}} = n_0 w/s$. In addition, the molecules sitting on the liquid–air interface interact on average (over the ensemble of local arrangements) with only half as many liquid molecules. We may neglect their interaction energy with the molecules of the gas,

since they only rarely encounter any of them. The cohesive energy of the molecules on this interface is thus $w_L/2$.

Note in passing that w_L is the energy one must supply to separate a molecule from all its neighbours, hence to evaporate the liquid. In fact, since each elementary separation involves two molecules, the energy required per molecule, that is, the *latent heat of evaporation* per molecule, is $\varepsilon' = w_L/2$.

When the area of the liquid–gas interface is increased, the number of molecules situated on this interface naturally increases too, while the other molecules remain completely immersed in the liquid. On average, each molecule initially immersed in the liquid and arriving at this interface loses a cohesive energy $w_L/2$, this being the elementary work that must be done on the system in order to achieve this operation. The total work that must be done to increase the area of the interface by an increment dA is $dW = (w_L/2)dA$. Defining the *interfacial tension*, usually known as the *surface tension* for a liquid–gas interface, by $\sigma_{LG} = w_L/2$, the surface energy that must be supplied to the system becomes

$$dW = \sigma_{LG}\, dA \ . \tag{2.33}$$

The surface tension of water in air at $20\,°\mathrm{C}$ is 0.073 Pa m. It changes by less than 10% around this value when the temperature goes from 0 to $50\,°\mathrm{C}$. For other liquids, it varies between 0.02 and 0.08 Pa m. This approach can be extended to two other arbitrary phases A and B in contact. It may then be useful to take into account the interactions between molecules in the two phases, which alters the definition of the interfacial tension σ_{AB} (see Sects. 3.2.3 and 6.2.1).

2.5 Solid State

2.5.1 Structures and Interactions

When we lower the temperature of a liquid, we thereby reduce the thermal agitation and hence also the possibilities for spontaneous relative motions of the molecules. In some cases, the structure remains disordered and we then obtain a glass (see Sect. 2.6). But in the most common situation with a simple body, the molecules arrange themselves into an ordered structure within which they continue to move slightly as a result of thermal agitation, but sit on average at some fixed position. In general, with the exception of water, the structure thereby obtained is denser than the liquid phase and the interaction energy of each molecule is significantly greater than in the liquid state. For a given pressure, this relatively sudden transition occurs at a specific temperature. However, in order for the transition to come about, it must start from a 'seed' that grows to take over the whole sample. In the same way, it is impossible to obtain the regular tiling of a mosaic by randomly pushing an ensemble of tiles around on the floor. One must start with a small set of tiles arranged according

to the chosen pattern. This structure can then be made to grow with the same pattern by successively placing the remaining tiles around the outside of this seed, an exercise that would soon get faster with the growth of the structure. Such a seed will often evolve close to a solid surface across which the molecules are more ordered, but in a liquid, it can also simply form around a suspended impurity.

The many possible characteristics of the resulting crystal structures are well known and we shall not go into the details here. For the record, the main ones are the hexagonal close-packed (hcp) and face-centered cubic (fcc) structures, which are the densest (74 %), with $n_0 = 12$ nearest neighbours for each atom, and the body-centered cubic (bcc) structure, which is less dense, with $n_0 = 8$.

In the above description, we only consider the special case of a solid formed by orderly arrangement of the same molecule as in the liquid phase. However, there are crystals in which the particles are atoms or ions, while in the corresponding gas, one finds molecules. The main kinds of interaction within a crystalline solid are:

- Simple van der Waals attractions, as in solid hydrogen, the noble gases, and alkanes. In this case, the atoms are simply juxtaposed.
- Ionic interactions, which are stronger, as in salt crystals like NaCl. Ions of opposite signs are arranged in such a way as to preserve charge neutrality.
- Covalent interactions, as in diamond or silica. These are giant molecules with oriented bonds. Their arrangement is determined by the valence number and directions.
- In metals, atoms release their valence electrons, leaving the ions in a sea of electrons. The forces between ions and electrons are key here, leading to a close packing with strong attractions.

Under such conditions and in order to simplify the discussion, we shall hereafter systematically use the term 'atom' to refer to the particles making up the basic structure of any solid.

2.5.2 Microrheology in the Solid Regime

In the solid state, the atoms are in equilibrium positions as regards their interactions with all the surrounding atoms. When a force is imposed on the material, the atoms are slightly displaced from these equilibrium positions. In this way, energy is stored in the system. When the force is removed, the atoms will naturally return to their original equilibrium position, i.e., the deformation is reversible. This is therefore essentially *elastic behaviour*.

To simplify here, we assume that each atom is in an equilibrium position with regard to the mutual interactions with each of its z nearest neighbours. Put another way, if the mutual interaction potential is Φ, this will have a relative minimum at a distance b equal to the separation between neighbouring atoms, whence $\Phi'(r = b) = 0$. When a force is applied to the solid, its atoms are slightly displaced relative to one another and the distance between the two atoms considered above is now r such that $|r - b| \ll b$. The interaction potential thus becomes

$$\Phi(r) = \Phi(b) + \frac{1}{2}(r-b)^2 \Phi''(b) + O\big((r-b)^3\big) \,. \qquad (2.34)$$

The force associated with this potential is

$$F = \Phi'(r) \approx (b-r)\Phi''(b) \,. \qquad (2.35)$$

An arbitrary deformation of the material will stretch or shorten the separation between the atoms by an amount $r - b$ that is proportional to this deformation. The constant of proportionality will depend only on the crystal structure and characteristics of the deformation. As a consequence, according to (2.35), the force required to impose a deformation will be proportional to this deformation. The total stress to be applied, equal to the sum of forces of this kind with different coefficients of proportionality, will also be proportional to the deformation. The material is thus *linearly elastic* in the limit of small deformations. In the following, we shall focus on the relationship between local physical characteristics and macroscopic properties of solids for specific simple deformations.

2.5.3 Elongation

Consider a solid cylinder with cross-sectional area A and length l to which a force F is applied at each end of the cylinder axis. The cylinder will then extend by an amount Δl. The deformation or strain is defined as the relative elongation $\varepsilon = \Delta l/l$ in the principal direction. The normal stress in the principal direction is the ratio $\sigma = F/A$ of the force to the cross-sectional area of the cylinder. Since we know that, for a small deformation, σ is proportional to ε, we define the Young's modulus of the material by

$$E = \frac{\sigma}{\varepsilon} \,. \qquad (2.36)$$

When the material is deformed in this way along a specific axis, it will also deform in the plane perpendicular to this axis. Indeed, the radius of the cylinder will change from R to $R + \Delta R$. If its volume is conserved, we have $\pi R^2 l = \pi (R + \Delta R)^2 (l + \Delta l)$. For small deformations $\varepsilon \ll 1$, it follows that $\Delta R/R = -\Delta l/2l = -\varepsilon/2$.

For convenience, we shall assume that, in this crystalline solid, the atoms are arranged in planes parallel to the cylinder axis and lined up in parallel lines a distance b apart in cross-sections perpendicular to the cylinder axis (see Fig. 2.13). There are l/b atoms along the cylinder axis and, as long as the cylinder deforms uniformly, no cross-section is favoured. Consequently, each atom is affected equally by the extension and thus moves a distance x relative to its neighbours, where $(l/b)x = \Delta l$. In the perpendicular plane, the atoms move a distance y such that $(R/b)y = \Delta R$, whence $y = x/2$. There are $1/b^2$ atoms per square metre in a cross-section perpendicular to the cylinder axis and the force applied to each atom is $f = Fb^2/A$.

Consider now the volume element bounded by two surface elements, as shown in Fig. 2.13 and separated by a distance b. When this volume is deformed by ε as
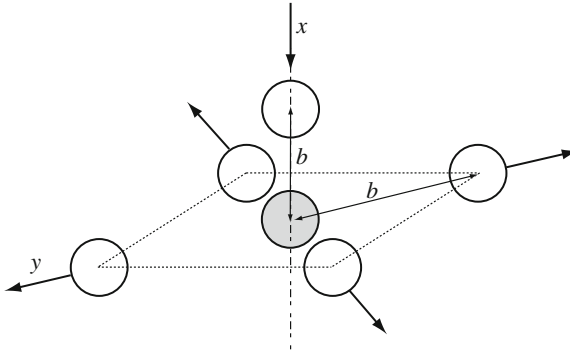
Fig. 2.13 Change in position of the atoms relative to a central atom (*grey*) under elongation. In this case, the atoms move closer together along the vertical axis and further apart in the perpendicular plane

described above, the particles are brought together in the direction of the x axis and moved apart in radial directions. The energy needed to do this is thus equal to the sum of the energy stored by bringing two atoms closer together (a central atom and four quarter atoms in the corners of the surface element) by a distance x, and by moving four atoms further away. According to (2.34), the total potential is to first order

$$\Psi = 6\Phi(b) + 2\frac{x^2}{2}\Phi''(b) + 4\frac{y^2}{2}\Phi''(b) \ .$$

We thus deduce the magnitude of the force in the x direction to be

$$f = \Psi'(x) = 3\varepsilon b\Phi''(b) \ .$$

Given the area $2b^2$ over which it applies, the Young's modulus is equal to

$$E = \frac{3}{2}\frac{\Phi''(b)}{b}. \tag{2.37}$$

2.5.4 Behaviour Under Simple Shear

Here we consider a simple shear inducing a deformation γ. For small deformations $\gamma \ll 1$, we know that the shear stress τ is proportional to the deformation, so we define the shear modulus by

$$G = \frac{\tau}{\gamma} \ . \tag{2.38}$$

Fig. 2.14 Displacement of
atoms distributed in parallel
planes under a simple shear in
the direction of one of these
planes. **a** Initial configuration.
b Configuration after a small
displacement y
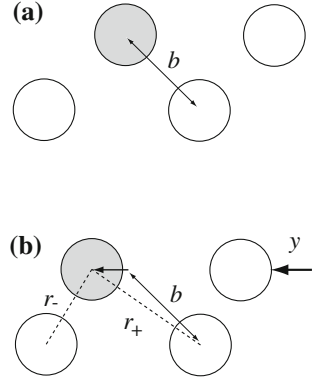
Suppose, for example, that the atoms are arranged in parallel planes and shifted
through an angle $\pi/4$ (see Fig. 2.14a). The structure is made up of atoms arranged
in a similar way in planes parallel to the one shown in Fig. 2.14, these planes being a
distance b apart. This is the same structure as the one discussed in Sect. 2.5.3. Since
the distance between two layers in the shear plane is $b/\sqrt{2}$, the deformation induces
a relative displacement $x = \gamma b/\sqrt{2}$ of the molecules in the principal direction. The
distance between two neighbouring molecules thus changes from $r = b$ to

$$r_{\pm} = \sqrt{\frac{b^2}{2} + \frac{b^2(1 \pm \gamma)^2}{2}} \ ,$$

where the plus and minus signs correspond to atoms moving apart or coming closer,
respectively (see Fig. 2.14b). For a small deformation $\gamma \ll 1$, we then obtain $r_{\pm} \approx
b(1 \pm \gamma/2)$. The macroscopic shear stress is the same as the shear stress obtained by
dividing the force f applied to each atom by the area $\sqrt{2}b \times b$ associated with it within
its layer, which gives $\tau = f/\sqrt{2}b^2$. If we only take into account the interactions of
the atom with its neighbours in the plane of observation, then according to (2.34),
the total interaction potential energy becomes

$$\Psi(x) = \Phi(r_+) + \Phi(r_-) = 2\Phi(b) + \frac{1}{2}x^2\Phi''(b) \ .$$

The magnitude of the force that must be applied to each molecule is then

$$f = \Psi'(x) = x\Phi''(b) \ ,$$

whereupon the shear modulus is

$$G = \frac{1}{2}\frac{\Phi''(b)}{b} \ . \tag{2.39}$$

We thus find that the shear modulus is 1/3 of the Young's modulus. This result, shown here for a specific crystal structure, turns out to be quite general, applying to any incompressible solid material.

2.5.5 Compressibility

In fact, this approach is not completely general because, when a material is deformed, it may succeed in minimising the energy supplied by collapsing in on itself to some extent. In particular, this implies that the material can be compressed when a uniform force, or pressure, is applied to it. This effect is described by introducing the *uniform compression modulus*, defined as the ratio between the imposed pressure and the relative reduction in volume $\omega = \Delta\Omega/\Omega$:

$$K = \frac{p}{\omega} \ . \tag{2.40}$$

Let us assume that the pressure causes all the atoms to approach one another by the same distance x. The force exerted on each atom is pb^2 and the work done is $pb^2 x$. The energy stored by a similar displacement of all the n_0 neighbours of the given atom and the interactions between the atoms is $n_0(1/2)x^2\Phi''(b)$. The energy associated with the volume $\Omega_m \approx b^3$ available around an atom is half of this since each interaction occurs in the volume associated with each atom. It follows that $p = n_0 x\Phi''(b)/4b^2$. In addition, the volume occupied by an atom can be written in the form $\Omega \propto 4\pi r^3/3$, where α is a coefficient depending on the atomic arrangement. Hence, $\Delta\Omega/\Omega = d\Omega_m/\Omega_m = 3x/b$ and finally,

$$K = \frac{n_0}{12}\frac{\Phi''(b)}{b} \ . \tag{2.41}$$

Note the similarity between the expressions for K and E obtained by the microscopic approach. In fact, there are quite general relations between these two parameters and they can be deduced using a macroscopic approach based on linear relations between stresses and strains (deformations):

$$K = \frac{E}{3(1-2\nu)} \ , \qquad G = \frac{E}{2(1+\nu)} \ , \tag{2.42}$$

where the Poisson coefficient ν introduces a correction that takes compressibility into account. For an incompressible material, we have $\nu = 1/2$, which implies that K is not defined since no compression is possible, and $G = E/3$. This is the situation for elastomers and most fluids. However, when the Poisson coefficient differs from 1/2, this means that the material can expand or contract. For most solids, ν lies between 1/4 and 1/3, implying a reduction in volume during elongation.
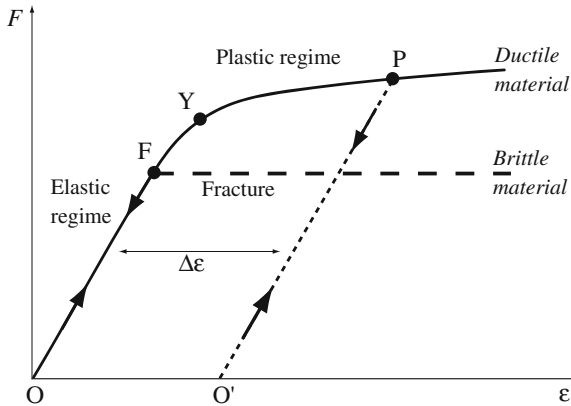
Fig. 2.15 Relation between force and deformation within the two main types of solid, namely, ductile and brittle

2.5.6 Maximal Mechanical Strength

The behaviour of a solid under significant deformation is not generally linear. One reason is that changes in the interaction potentials are more complex for large relative motions of the atoms. Another is that, for imperfect crystals, some bonds may actually break. It is not easy to treat this regime in a completely general way. When a solid is deformed still further, e.g., under traction, two kinds of behaviour are observed in practice (see Fig. 2.15):

- **Ductile Materials.** These can be quite significantly deformed without fracture, the deformation increasing with the applied stress. For small deformations (OY in Fig. 2.15), the behaviour is linear elastic to begin with. The deformation is reversible if the stress is removed, but beyond a critical deformation (associated with the point Y), further deformation is in part irreversible. This is the ductile (or plastic) regime. If the stress is removed, for example beyond the point P, the system does not return along the curve PO, but instead the deformation decreases along the curve PO′. If the stress is once again increased starting from the point O′, the system climbs back along the same curve, indicating that the behaviour is indeed elastic in this regime, but that the material has undergone an irreversible (plastic) deformation $\Delta\varepsilon$.
- **Brittle Materials.** These deform elastically up to a critical value of the deformation (associated with point F in Fig. 2.15), or equivalently, a critical value of the stress beyond which the material fractures, i.e., it separates into two pieces whose elements no longer interact as they did in the uniform material. This behaviour is represented by the dashed horizontal straight line in Fig. 2.15.

It is interesting to estimate the critical stress corresponding to the transition to plastic deformation for a ductile material or corresponding to fracture in the case of a brittle

material, since this critical stress represents the maximum resistance of a material to deformation. Even though the two phenomena look different macroscopically, one would expect them to occur for similar reasons, precisely when we induce a structural modification which takes it beyond the point of no return.

2.5.6.1 Ductile Solid

Consider the situation depicted in Fig. 2.14. A simple shear is imposed on a material made up of atoms distributed in plane layers parallel to the shear direction. As we have seen, the deformation causes some atoms to come closer together and others to move further apart, and the interaction potential energy increases. This phenomenon continues until the displaced atom reaches the level of the neighbouring atom in the lower layer and continues on its way toward a position equivalent to its initial position, but situated between the two atoms of the lower layer. In this last step, the potential energy drops back down to its minimal value again. There is therefore a critical deformation γ_c, of the order of 1/4 in our example, beyond which it is no longer necessary to apply a force to maintain the deformation. The structure subsequently evolves on its own toward a new configuration associated with the shift between the two layers. If we maintain the force required to achieve this critical deformation, we can thus in principle displace one layer of atoms indefinitely relative to the other layer, by a succession of jumps like the one just described. The corresponding critical stress, which is in fact associated with the point of inflection of the potential energy curve, can be estimated roughly if we assume that the material has the same shear modulus (determined in the linear regime) right up to the critical deformation, whence

$$\tau_c \approx G\gamma_c . \tag{2.43}$$

In practice, it turns out that this seriously overestimates the actual value, by a factor of the order of 100 or 1,000. The above analysis can be corrected by taking into account the decrease in the shear modulus when the deformation increases, but this cannot reduce the value of the critical stress as much as necessary. We must therefore look for another explanation for this discrepancy, namely, localised weak points in the material called *dislocations* which facilitate collective movements of the atoms. These dislocations take the form of atomic planes partially inserted between two layers. For a shear in a direction perpendicular to these planes, a much smaller stress than the one needed for extraction from a potential well is sufficient for the inserted plane to slide along and position itself opposite some other plane. Moreover, the resulting lateral shift is nevertheless of order b, which means that small stresses can generate significant deformations. However, the adaptation of this argument to explain the full deformation of the material is a complex matter that goes beyond the scope of this book.

Fig. 2.16 Irregularity or
'hole' at the surface of a solid,
leading to the formation of a
fracture under traction
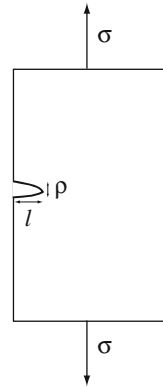
2.5.6.2 Brittle Solid

For a brittle material, fracture occurs when two atomic layers literally come apart. In this case, the simplest thing to consider is the effect of traction. Once again, the applied force must first increase with distance, but then drops off rapidly beyond the inflection point of the potential. Assuming as before that Young's modulus remains constant over this broad range of deformations, we find that the critical stress is of the order of $\sigma_c = \gamma_c E$, with γ_c of the order of 1/4. Taking into account the dependence of Young's modulus on the deformation, we would obtain a slightly smaller critical stress, but nevertheless much greater than the actual value, by a factor of 10–100. At this point, one must consider local weak points within the material in order to explain this result.

It is irregularities on the outer surface of the solid that lead to these weak points. For example, if there is a small hole at the surface of the solid (see Fig. 2.16), the local stress near the bottom of the hole is much higher than the macroscopic stress. A detailed calculation assuming the material to be linearly elastic shows that, for a hole of radius r and depth l, the stress at the bottom of the hole is

$$s = \sigma \left(\frac{l}{r}\right)^{1/2} , \tag{2.44}$$

where σ is the stress applied to the sample. Since the ratio l/r is generally large, this can lead locally to a very high stress, close to the theoretical value expected from the above estimates, and hence capable of generating a fracture that subsequently propagates through the material. And all this while the macroscopic stress remains rather low.

2.5.7 Solid–Liquid Transition

As the temperature of a solid is increased, so also is the agitation of its constituent molecules. The molecules at the surface are in the shallowest potential wells since they are bound to fewer molecules than their counterparts within the material, so it is naturally these molecules that are first to leave the solid state. This happens at a slightly lower temperature than the temperature referred to as the solid–liquid equilibrium temperature. A liquid layer thus forms at the free surface of the solid. At the solid–liquid equilibrium temperature, the liquid phase moves gradually through the material as more heat is supplied to the system. By thus increasing the temperature, we increase the amplitude of agitation of the molecules about their equilibrium position in the solid state, until this amplitude is such that the ordered structure can no longer maintain itself. For a crystal, this happens when the amplitude of agitation reaches about 20 % of the distance between the closest molecules within the structure.

2.5.8 Solid–Gas Transition

The *latent heat of sublimation*, that is, the energy required to vaporise unit mass of solid material, can be related to a first approximation to the cohesive energy $w_S = n_0 w$ between the atoms. The calculation is similar to the one for the latent heat of evaporation (see Sect. 2.4.6). The energy needed per molecule to completely separate all the molecules from one another, that is, the sublimation energy, is

$$L_S = \frac{1}{2}w_S \ . \tag{2.45}$$

For materials like neon, argon, and krypton, this calculation gives a value very close to the actual value. For other materials, things are more complicated. For example, for ionic solids, sublimation preserves the interaction between certain atoms, e.g., Na and Cl, and for metals, the interactions between electrons must be taken into account. It turns out that L_S usually lies between 1/3 and 1/6 of the interaction energy w_S between the basic elements of the structure.

It is interesting to note that the latent heat of fusion is roughly 1/10 of the latent heat of sublimation, which suggests that fusion leads to a slight decrease in the number of bonds. As it happens, there is no precise physical justification for this result. We may just say that, qualitatively, a certain energy is needed to provoke the molecules to the point where the system liquefies, but much more energy is needed to remove them completely.

2.6 Glassy State

2.6.1 Glasses

Most mineral elements form liquids with rather low viscosities when they melt. Conversely, when the temperature is lowered, these liquids crystallise rapidly once below the melting point, thereby solidifying, and this even if the cooling rate is very fast. However, there are materials which give liquids with relatively high viscosities when they melt, of the order of 10^4–10^6 Pa s. When such materials are cooled quickly enough, any crystallisation can be totally avoided. The viscosity of the liquid increases steadily to reach such values that the material may be considered as a solid. Such materials are *glasses* (or *amorphous materials*) and the phenomenon leading to this type of material is called the *glass transition*. Various materials have a glassy phase, including oxides such as SiO_2 and Na_2O, sulfides, phosphorus, organic molecules like toluene, methanol, glucose, or sucrose, polymers (see Chap. 3), and metallic glasses if the cooling is fast enough.

The structure of a glass is similar to that of a liquid in that the molecules or atoms are very close to one another and there is no long-range order. On the other hand, as in a solid, the atoms or molecules are not free to move very much relative to one another, their displacements being limited to the tiny motions around their average positions resulting from thermal agitation. In terms of its internal structure, one may thus view a glass as a rigidified liquid.

2.6.2 Glass Transition

Experimentally, this transition can be monitored via changes in the volume of the material when the temperature is varied at constant pressure. When a liquid is cooled, its volume first decreases steadily, following branch A corresponding to liquid behaviour. When the crystallisation temperature T_S is reached, the volume drops suddenly and the system evolves along branch B corresponding to solid behaviour. In some cases, the liquid can nevertheless be cooled below T_S without it crystallising, either because it has been cooled very quickly, or because its molecular characteristics prevent it from crystallising. In this situation, the liquid evolves along branch A. Then at a certain temperature T_{g1}, there is a sudden change in the slope of the curve due to a change in the behaviour of the system. This is the *glass transition temperature*. In fact, for a given liquid, this temperature is not unique, but depends on the cooling rate. For example, cooling the system more slowly, the transition will occur at a temperature $T_{g2} < T_{g1}$. Note that, if we carry out experiments with slower and slower cooling rates, the glass curve ends up coinciding with the crystal curve. This occurs at a critical temperature T_k called the Kauzmann temperature, which is the lowest glass transition temperature than can be reached for the given system.
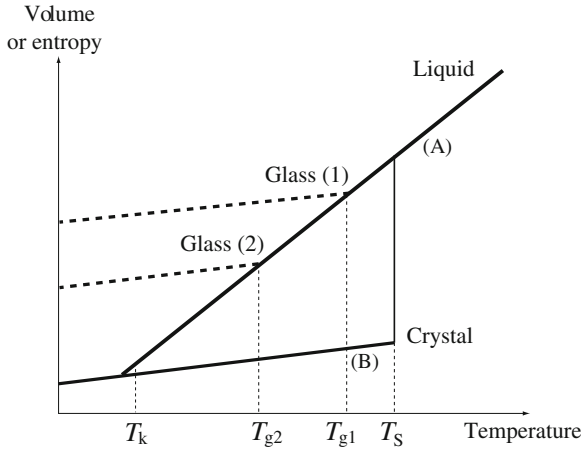
Fig. 2.17 Glass transition. Temperature dependence of the entropy or volume for different types of material or different cooling rates

In practice, the glass transition is usually studied by monitoring changes in the specific heat. The glass transition is then characterised by a drop in the specific heat. Since the specific heat at constant pressure is related to the entropy by

$$c_p = T \left. \frac{\partial S}{\partial T} \right|_p ,$$

the temperature dependence of the entropy of the system can be found by integration. This dependence is qualitatively similar to that of the volume (see Fig. 2.17).

It is thus observed that the entropy of a glass remains finite even when the temperature tends to zero. Glasses therefore have a residual configurational entropy which reflects the level of disorder. It is also observed that the entropy of a glass is not a simple thermodynamic state function, since it turns out that it depends on the temperature and pressure history of the sample. This means that, in a glassy state, the material is no longer able to explore all possible microscopic states, and one speaks of ergodicity breaking.

2.6.3 Mechanical Behaviour Associated with the Glass Transition

Regarding the question of mechanical behaviour, a glass cannot simply be considered as an extremely viscous liquid. Indeed, under ordinary observation conditions, glasses have certain properties that are commonly found in solids, and in particular a nonzero elastic modulus. This type of behaviour has already been mentioned for liquids, but over extremely short time scales (see Sect. 2.4.3). When considering glasses, one

Fig. 2.18 Viscoelastic
behaviour. Two phases in
the time dependence of the
deformation, for fixed stress
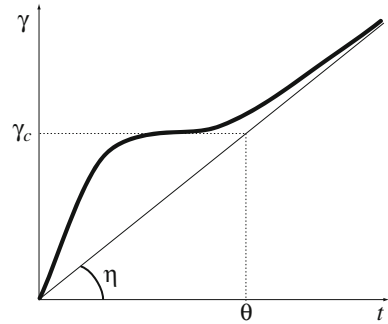
must thus envisage some kind of intermediate form of matter that can behave under
ordinary conditions either like a solid or like a liquid, depending on the circumstances,
that is, depending on the boundary conditions or conditions of observation. In a
physically consistent description, they can conveniently be considered to exhibit
viscoelastic behaviour.

When subjected to a stress τ from some initial time (and assuming that it was at
rest up until then), a viscoelastic material reacts to begin with like an elastic solid. The
resulting deformation is finite, increasing with the applied stress, and the initial shape
is recovered when the stress is removed. However, if the applied force is maintained
beyond some characteristic time (which we shall soon find to be the relaxation time
θ), the material will deform more easily and in fact the deformation will end up
increasing linearly in time (see Fig. 2.18), i.e., the material will begin to flow like a
liquid. If the solid regime is roughly characterised by a constant elastic modulus G
and the liquid regime by a Newtonian viscosity μ, the transition between the two
regimes occurs somewhere near the intersection between the deformation plateau
$\gamma = \tau/G$ of the solid regime and the straight line $\gamma = \dot{\gamma}t = \tau t/\mu$ corresponding
to flow in the liquid regime. It follows that this solid–liquid transition occurs after a
time equal to a characteristic time θ such that $\tau/G = \tau\theta/\mu$, i.e.,

$$\theta = \frac{\mu}{G} \ . \tag{2.46}$$

In fact, this is the behaviour of a liquid such as we have described it qualitatively,
with a very short characteristic time. Extending the analogy, this suggests that the
relaxation time θ is the characteristic time for spontaneous reorganisation of the
material through thermal agitation.

The above relation is particularly interesting because it shows that, if the elastic
modulus does not change too much with temperature, and this seems realistic enough
since the thermal agitation is not directly involved in the behaviour of the system in
its solid regime, the viscosity of the material must exhibit the same variations as the
relaxation time under changes of temperature.

It should nevertheless be borne in mind that this is a very rough description of the reality since it does not take into account a range of features observed in glasses. For example, it seems that several relaxation times must be taken into account to describe the time dependence of a deformation. In addition, fracture phenomena and localisation phenomena suggesting plastic behaviour have been observed.

2.6.4 Viscosity of Glasses

Given a reduction in thermal agitation, one must expect the relaxation time of the system, and hence also its viscosity, to increase when the temperature is lowered. In practice, it turns out that the relaxation time increases suddenly above the temperature T_g. In fact, relaxation phenomena in glasses can rarely be described in terms of a single relaxation time. As a consequence, the simplified description above is not strictly valid. In reality, the time required to reach equilibrium, corresponding to the longest relaxation time, is significantly longer than the experimental time scale, which means that we are dealing with a *non-equilibrium system*. However, in the largely qualitative discussion below, we shall assume that the system has only one relaxation time.

Empirically, it is found that the viscosity of glasses, when represented in a plot of $\log \eta$ versus T_g/T, follows a curve that seems to diverge at T_g. In this particular context, T_g is arbitrarily defined as the temperature at which the viscosity reaches a value of 10^{13} Pa s. In this same kind of plot, different glassy materials do not give the same curves. For the strongest materials, typically composed of tetrahedral lattices like SiO_2, the curve can be quite well represented by a straight line, whence the model used to describe them has the form

$$\mu = \mu_0 \exp \frac{E_a}{RT} \; . \tag{2.47}$$

For brittle materials, usually ionic or molecular liquids, the curve has a slope that increases steadily and tends to a vertical asymptote when $T_g/T \to 1$. One model used to describe this behaviour is the so-called Vogel–Fulcher–Tammann–Hesse model:

$$\mu = \mu_0 \exp \frac{B}{T - T_0} \; . \tag{2.48}$$

The existing rheophysical description of glasses (free volume, cooperative motion, and mode-coupling models) is still largely based on rather speculative or relatively technical theories which go beyond the scope of this book.

Further Reading

1. Cabane, B., Hénon, S.: Liquides—Solutions, dispersions, émulsions, gels. Belin, Paris (2003)
2. Cottrell, A.H.: The Mechanical Properties of Matter. Wiley, New York (1964)
3. Guinier, A.: The Structure of Matter: From the Blue Sky to Liquid Crystals. Butterworth-Heinemann Ltd, Oxford (1984)
4. Israelachvili, J.: Intermolecular and Surface Forces, 2nd edn. Academic Press, London (1991)
5. Jancovici, B.: Statistical Physics and Thermodynamics. McGraw-Hill, New York (1973)
6. Jones, R.A.L.: Soft Condensed Matter. Oxford University Press, Oxford (2002)
7. Loeb, L.B.: Kinetic Theory of Gases. McGraw-Hill, New York (1927)
8. Tabor, D.: Gases, Liquids and Solids, 3rd edn. Cambridge University Press, Cambridge (1991)
9. Zarzycki, J.: Glasses and the Vitreous State. Cambridge University Press, Cambridge (1991)