

Materials science for biomedical engineering

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MATERIALS SCIENCE FOR BIOMEDICAL ENGINEERING

SECOND EDITION



MARCEL VAN GENDEREN

**Materials Science
for
Biomedical Engineering**

Materials Science for Biomedical Engineering

2nd edition

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For Marie-Thérèse

Acknowledgements

First edition

This book was written over a number of years. It started when I took over the Materials Science class, and looked for an appropriate book for Biomedical Engineering students. There wasn't one. Then I decided on a reasonable book, to which I added notes on the topics I thought were missing. This turned out to be quite confusing for the students, so I started working on expanding my notes with the parts of the book that I needed. At that point, Bert Meijer said: "You should write a book", and it is now finished because he gave me the opportunity to do it. Thanks for that, Bert. Also, credit should go to Fons Sauren for continuously (but gently) pushing me to finish it. Leon Govaert gave me a good idea for a way to structure the whole class. The terrific books of J.E. Gordon (see Appendix D) helped me a lot: they made me understand what it was all about. The Biomedical Engineering students during several years must be thanked for critical reading of the various incarnations of my notes, and for trying to understand what I wanted to tell them. Several students helped me with proofreading and making the figures, especially Jeroen Hamers and Evelinda Baerends. Of course, all errors that are undoubtedly still in this book are my responsibility.

*Marcel van Genderen
October 2005*

Second edition

For the second edition, many errors, inconsistencies and unclear passages were found by the Biomedical Engineering students using this book: many thanks to them! Especially Bart Spronck and Stijn Aper were very helpful. Also, some of the symbols have been changed to agree with the new Biomechanics book of Oomens, Brekelmans and Baaijens. Any mistakes that still remain in this edition are of course completely due to me.

*Marcel van Genderen
May 2008*

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All our science, measured against reality, is primitive and childlike—
and yet it is the most precious thing we have.

Albert Einstein
(1879–1955)

Before we start

Why do biomedical engineers need to know about materials science? Mostly, books about materials science are concerned with constructing bridges or building planes, and involve the use of concrete and steel. Newer applications of materials science are found in the solid-state devices for micro-electronics, where one needs to know how to work with semiconductors, or the development of advanced polymeric materials for a variety of purposes.

From an engineering viewpoint, the human body is a (magnificently complex) construction with an advanced control system built-in. If we want to understand this construction, how it is built, how it behaves, and especially if we want to modify, repair, or improve it, we need to know something about the basics of the materials that are found in the human body and of the materials that we want to put in there. We will see that we can use a lot of knowledge that mechanical engineers have acquired, but that we will also need other areas of science (chemistry, biochemistry, biology) in order to understand the human body from a mechanical engineering viewpoint.

General information

In this book we will look at the relation between the structure of materials and their mechanical properties. This needs parts of various scientific disciplines: chemistry, physics, mechanics, and biochemistry. Unfortunately this information was up to now not available in one textbook. The present book is based on several books that are worth studying by themselves for further explorations in materials science (listed in Appendix D).

Words that are printed **bold** (except this one, of course) are listed in the Glossary (Appendix A). Usually, bold is only used in the section where the term is defined or discussed in most detail.

In formulas, units of quantities will be given between square brackets if necessary to avoid misunderstanding, e.g. energy: E [J].

Overview of the book

As mentioned in the previous section, the main objective of this book is to show the relation between the structure of a material and its mechanical properties. We will see that we need to look at the structure, not only at the level of atoms and bonds (microscale), but also on a larger scale where we can see the imperfections in the material (mesoscale). As engineers, you must be able not only to explain the relation between structure and properties, but also to perform calculations on several aspects of both structures and properties.

After an introduction to materials and the definition of various terms in Chapter 1, we will first take a look at the relevant mechanical properties (Chapter 2). Then, in Chapter 3, we will look at the only mechanical property that can be derived from the atomic (microscale) structure: the modulus of elasticity.

In the rest of the book, we need to look at both the micro- and mesoscale structure in order to understand the mechanical (macroscale) properties. Therefore, there will always be a Chapter on structure, followed by a Chapter on properties.

First, we will look at the materials that are based on strong covalent or ionic bonding, and that usually form crystalline structures: the inorganic materials (Chapters 4 and 5).

Then, we will study the materials that are based on macromolecules with weak intermolecular bonds: the polymers and biopolymers (Chapters 6 and 7), which are usually partly crystalline and partly amorphous.

In the final two Chapters, we will look at ways to change the properties of materials: various processing techniques to change the structure (Chapter 8), and the making of composite materials (Chapter 9). Also, we will take a first look at bio-composites, which occur a lot in the human body.

Most Chapters have problems associated with them, and answers are given in Appendix O. Problems indicated with * are typical for the degree of difficulty to be expected in examinations. There are also various Appendices with important data that you will need for making the problems, so take a look at them.

There are various Intermezzos in the text: these are extra, and do not belong to the material that will be tested.

1 Introduction

Materials are in general all solids, so this book will deal with various kinds of solid materials.

Materials can be looked at from various perspectives, and in this chapter we will take a look at the ones that are most useful to us.

By doubting we come at truth.

Marcus Tullius Cicero
(106–43 BCE)

1.1 Length scales

Materials of course have many types of properties (electrical, magnetic, optical, thermal...), but in general it is possible to assign them to typical classes: metals, (bio)ceramics (and glasses), and (bio)polymers. Here, we will concentrate on the relation between the **mechanical properties** of a material and its structure. Mechanical properties will include elasticity and strength in terms of tension and compression, twisting, shearing, and bending.

In order to understand the relation between the mechanical properties of a material (**macroscale**: a length scale of > 1 mm) and its structure, we will see that we need to look at the structure not only at the level of atoms and bonds (**microscale**: length scale of ca. 1 nm), but also on a larger scale where we can see the imperfections in the material (**mesoscale**: length scale of ca. 1 μ m). This is illustrated in Figure 1.1.

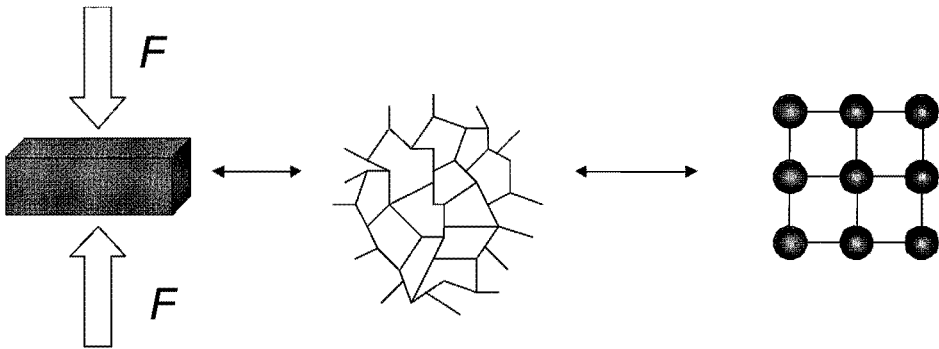


Figure 1.1. From macroscale to mesoscale to microscale.

1.2 Materials classification

There are several ways to classify materials, but not all are useful for us here: e.g. the chronological classification (wood and bone, stone, copper, bronze, iron, steel, plastics). In the following paragraphs we will look at some important classifications and aspects of materials.

1.2.1 Natural vs. synthetic materials

Nature uses a rather restricted set of building blocks for materials. Synthetic materials in general are stronger and stiffer than natural materials, but they also have a higher density. Composites can combine the best of these properties. Natural materials have a highly optimized construction compared to synthetic materials, they can grow in place instead of being manufactured, and they can be repaired.

1.2.2 Engineering materials vs. biological materials vs. biomaterials

Most books about materials treat the engineering materials (steel, concrete): they are used to build bridges and airplanes. In this book we will limit ourselves mostly to:

(i) synthetic materials that can be used in the human body. These are by definition **biomaterials: polymers**, such as nylon, silicones, Teflon and Dacron; **metals**, such as titanium, steel, Co/Cr-alloys and gold; **ceramics**, such as alumina (Al_2O_3), carbon, and hydroxyapatite; and **composites**;

(ii) **biological materials** that are in the human body (**proteins, polysaccharides, bioceramics**), or that can be used as biomaterials in a modified form (spider silk, collagen).

Biological materials can be very complex: tissues, muscles, extracellular matrix, etc. We will only be able to look at them briefly in this book.

1.2.3 Simple materials vs. composites & structures

Monolithic materials (whole structure is one material) are much simpler to understand, but composites (combinations of materials) are more relevant for modern and biological materials. Therefore we will start with monolithic materials, but move to composites later on in the book.

Hierarchical and **cellular** materials or structures—the difference is less clear here—are especially important in biological systems: there are various levels of construction, which all influence the material's properties.

Examples of hierarchical systems are tendon (Figure 1.2) and bone, while bone also is a composite material.

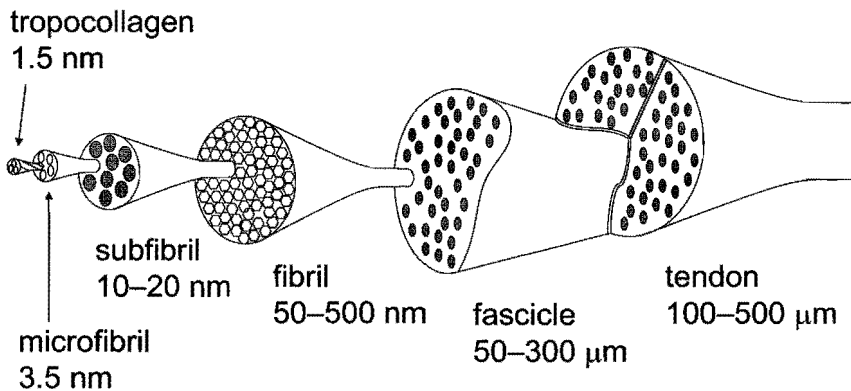


Figure 1.2. A hierarchical structure occurring in the human body.

Cellular materials or structures are built up from open spaces and thin walls, and are found both in nature (such as cork) and in synthetic materials (think of bubble plastic).

1.2.4 Types of chemical bonds

Atoms or **molecules** have to stick together to form materials. This can occur via strong chemical bonds, or via weaker secondary interactions. The strong bonds are either based on **electrostatic** attraction between oppositely charged ions, or on shared electrons in **covalent** bonds.

The secondary interactions are all based on permanent or transient dipoles. The weakest interaction is the **van der Waals attraction**, which is always present, even between completely apolar molecules. A stronger attraction is caused by **dipole–dipole interactions** between polar molecules. The presence of an O–H or N–H group leads to **hydrogen bonds**, which are the strongest secondary interactions.

Atoms can form bonds via electrostatic (Coulomb) interactions when they lose or gain electrons to form **ions**. This leads almost always to crystalline compounds (**salts**) where the cations and anions are stacked in a regular lattice. Salts are a form of ceramic materials.

Atoms can also form covalent bonds by overlap of orbitals. This can lead to: (i) the formation of small or large molecules (see below), or (ii) the formation of a **covalent network**, which is already a material (e.g., diamond; silicon). These latter materials are also ceramics.

A special kind of covalent network is seen for the metals: they do not form individual bonds between atoms, but form one large molecular orbital for all atoms in a piece of material: the **metallic bond** or electron “sea”.

Small and large molecules can form a material via intermolecular interactions: van der Waals, dipole–dipole, hydrogen bonding and electrostatic interactions. Since these secondary interactions are rather weak, this will not lead to useful materials, unless the molecules are very large (**macromolecules**) and there are many interactions that add up. These materials are the **(bio)polymers**.

1.2.5 Biomedical aspects

For biomaterials there are a number of aspects that are not important for the normal engineering materials: biocompatibility, sterilization, cell and protein adsorption, biodegradation/erosion, bioinertness, bioactivity, toxicity, carcinogenicity, thrombogenicity, immunogenicity. These aspects require knowledge of biology and biochemistry besides materials science. We will not be able to treat them all here, but in several places we will mention material properties that are important in biomedical engineering.

1.2.6 Bulk vs. surface

There are large differences in composition, and therefore also in properties, between the surface of a material and its **bulk** (the “interior” or average). For biomaterials, this is especially important, since the interaction between material and human body occurs at the surface of the material. Therefore this is important for a lot of the biomedical aspects mentioned in the previous section.

2 Mechanical properties

In order to be able to speak about properties as strength and stiffness, we should first look at a bit of mechanics. We shall see that especially the term “strength” is very vague, and should always be replaced by something more specific.

We will only discuss mechanical behaviour of deformation in one direction.

Science is a long history of learning how not to fool ourselves.

Richard Feynman
(1918–1988)

2.1 Elastic behaviour

Elastic deformation occurs when a force deforms a material, but after the force is removed, the original shape returns: it is reversible.

2.1.1 Definitions of stress and strain

Deformation of a material can occur in various ways, depending on the direction of the force applied to it. As can be seen in Figure 2.1, forces on a material (F [N]) can lead to various types of deformation.

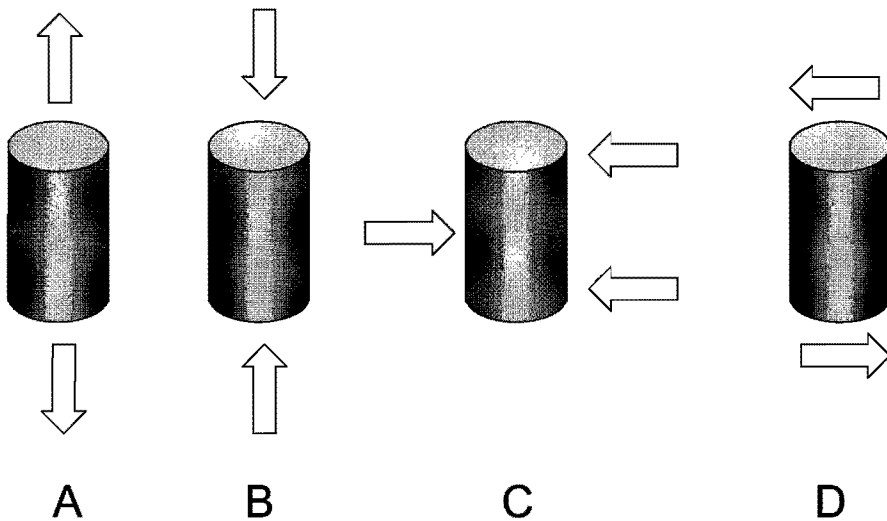


Figure 2.1. Different orientations of the force on a material can lead to tension or elongation (A), compression (B), bending (C) or shearing (D).

However, the force depends on the size of the material objects we are testing (thinner test bar: less force necessary). Therefore we always use **stress**, which is force per unit of area. For **tension** and **compression**, the area in question is perpendicular to the force, and we use:

$$\sigma = \frac{F}{A_0} \text{ [Pa]}$$

A_0 is the area of the original cross section of the tested material. In Figure 2.2 we see a typical elongation due to a tension stress. The cross section may have a different area after the elongation (A), but we will look at that effect later in detail.

In order to describe what is happening to the dimensions of the material when a force is applied, we look first at the length change during tension or compression:

$$\Delta L = L - L_0 \text{ [m]}$$

However, this ΔL is dependent on the length of the test bar, so we use the dimensionless quantity **strain**:

$$\varepsilon = \frac{\Delta L}{L_0} [-]$$

Another dimensionless quantity that is often used is the **elongation factor** (or stretch):

$$\lambda = \frac{L}{L_0} = 1 + \varepsilon$$

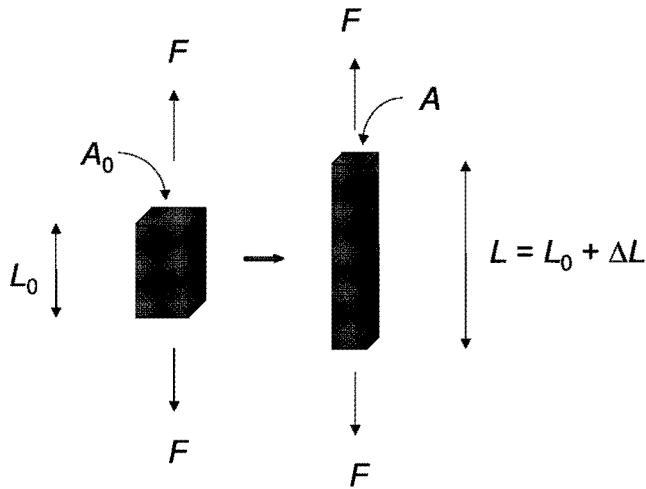


Figure 2.2. Effect of a force in tension.

For **shearing** (see Figure 2.3), the area we use for A_0 is parallel to the force, and we write for the **shear stress**:

$$\tau = \frac{F}{A_0} [\text{Pa}]$$

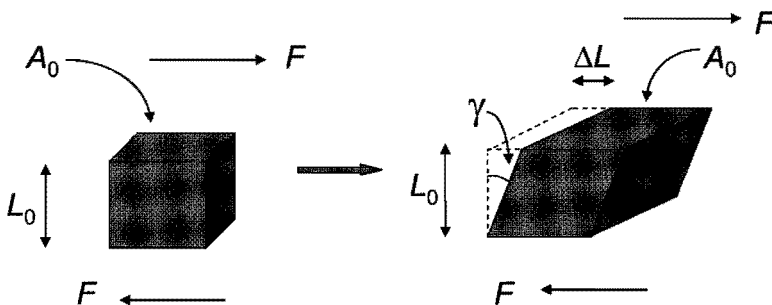


Figure 2.3. Effect of a shear force.

For shearing forces, we calculate the change in dimensions via the **deformation angle**:

$$\gamma \approx \tan \gamma = \frac{\Delta L}{L_0} \text{ (for small deformations, and } \gamma \text{ in rad)}$$

Now, L_0 is perpendicular to ΔL .

Intermezzo

A special type of deformation comes from hydrostatic pressure (p [Pa]): the force is now the same from all directions.

For hydrostatic pressure, we look at the change in volume:

$$\varepsilon_V = -\frac{\Delta V}{V_0}$$

2.1.2 Elastic deformation

Elastic deformation occurs when the material returns to its original shape after the force is released, like a spring: the deformation is reversible. This means that we are only stretching or compressing the chemical bonds in the material, without breaking them. For elastic materials, **Hooke's law** holds:

$$\sigma = E\varepsilon \text{ for tension and compression}$$

$$\tau = G\gamma \text{ for shearing}$$

Here, E is the **Young's modulus** ([Pa]), or modulus of elasticity, and G is the **shear modulus** ([Pa]). Both are a measure of the **stiffness** of a material: the resistance to elastic deformation. Both E and G are material properties, and can be found in tables (see e.g. Appendix E).

We will see later that the stiffness is not always the same for tension and compression. For several compounds, tension is not always the most practical way to test stiffness, so bending (**flexural stiffness**) is often used.

Intermezzo

In fact, stiffness is a property of a piece of material: when a force F gives a length change ΔL , the stiffness is $F/\Delta L$ [N/m]. The Young's modulus is a material property, and is related to the stiffness as $E = \text{stiffness} \times L_0/A_0$.

Intermezzo

Compression due to hydrostatic pressure gives a bulk modulus K :

$$p = -K \frac{\Delta V}{V_0}$$

2.1.3 Poisson ratio

The **Poisson ratio** (ν) is used to measure the change in cross-sectional area during deformation, since there is also strain (usually negative: compression) in the x - and y -direction when we stretch a material in the z -direction. For **isotropic** materials, we can write:

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\varepsilon_y}{\varepsilon_z}$$

(For a cylinder, the change in the diameter is used: $\varepsilon_x = \varepsilon_y = \Delta d/d_0$.)

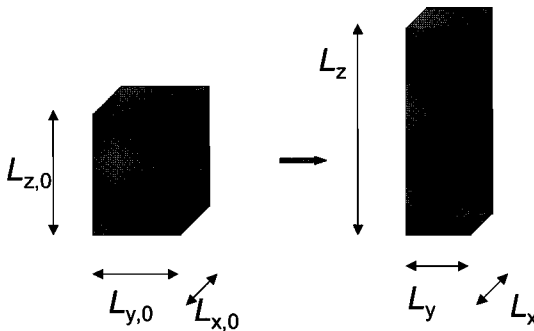


Figure 2.4. Change of all dimensions after deformation due to a tensile stress.

The volume of the material after deformation can be calculated now, since we know how the dimensions change (see Figure 2.4):

$$L_x = L_{x,0}(1 + \varepsilon_x)$$

$$L_y = L_{y,0}(1 + \varepsilon_y)$$

$$L_z = L_{z,0}(1 + \varepsilon_z)$$

$$V = L_x L_y L_z = L_{x,0} L_{y,0} L_{z,0} (1 + \varepsilon_x)(1 + \varepsilon_y)(1 + \varepsilon_z)$$

Using the Poisson ratio this becomes:

$$V = V_0 (1 - \nu \varepsilon_z)^2 (1 + \varepsilon_z) = V_0 \{1 + (1 - 2\nu)\varepsilon_z + \nu(\nu - 2)\varepsilon_z^2 + \nu^2 \varepsilon_z^3\}$$

$A = \text{root of } 1 - \nu \varepsilon_z$

For small values of ε_z (as is usually the case for elastic behaviour) this gives approximately:

$$\frac{\Delta V}{V_0} = \frac{V - V_0}{V_0} = (1 - 2\nu)\varepsilon_z$$

This means that for $\nu = 0.5$, the volume of the material will not change during tension or compression, which is often assumed to make things easy. This is typical for rubbers: they can easily change shape.

If $\nu = 0$, then ΔV is large, since you can stretch the material while its cross-sectional area stays constant. This usually means that the bonds between atoms are very strong, so you cannot stretch very far.

For most materials $\nu = 0.2$ – 0.3 : an intermediate situation where $\Delta V/V_0$ is ca. $0.4\varepsilon_z$ to $0.6\varepsilon_z$. Since most materials cannot be stretched elastically very far, this is not a large effect.

Example: Aluminium alloys have $\nu = 0.3$, and can be stretched elastically only up to $\varepsilon = 0.005$. This means: $\Delta V/V_0 = 0.002$ at most (0.2%).

The following relation holds for the various measures for stiffness:

$$G = \frac{E}{2 + 2\nu}$$

This means that for the usual assumption of $\Delta V = 0$ ($\nu = 0.5$), we get: $E = 3G$.

2.2.4 Elastic energy

When we plot stress versus strain, elastic deformation will be a straight line ($\sigma = E\varepsilon$). The area under this line is the energy that is necessary to deform 1 m^3 of the material up to strain ε :

$$E_{\text{el}} = \frac{\sigma\varepsilon}{2} = \frac{E\varepsilon^2}{2} = \frac{\sigma^2}{2E} \quad [\text{Pa}] (= [\text{N/m}^2] = [\text{J/m}^3])$$

Since the deformation is reversible, this energy is stored in the material like in a spring: it is released when we remove the force. The maximum elastic energy that can be stored in a material is called its **resilience**. This maximum is reached upon fracture or yield (see next section).

2.2 Tensile test: plastic behaviour, fracture

Some materials, like ceramics, break when they reach the limit of elastic deformation. Most metals and polymers can be deformed further, but this deformation will not go away when the force is removed: it is a permanent, **plastic deformation**. We are then breaking chemical bonds in the material, and forming them again in a different position. To do this costs more energy, and is not reversible. However, it does not break the material.

The change from the elastic region to the plastic region is called **yield**. In the stress–strain curve there is a stress where yield occurs, which is called the **yield strength** or **yield stress** (σ_Y), and an associated **yield strain** (ϵ_Y). What is the difference here between stress and strength? The stress is something we apply from the outside, but seen as a material property it is called strength.

The stress–strain curves for the different types of materials are quite different: in Figure 2.5 we can see how ceramics show brittle fracture after elastic deformation (A); some metals and polymers will show yield and then fracture (B); other metals and polymers can be plastically deformed very far after yielding (C); and rubbers can be stretched elastically, but the relation between stress and strain is not linear (D).

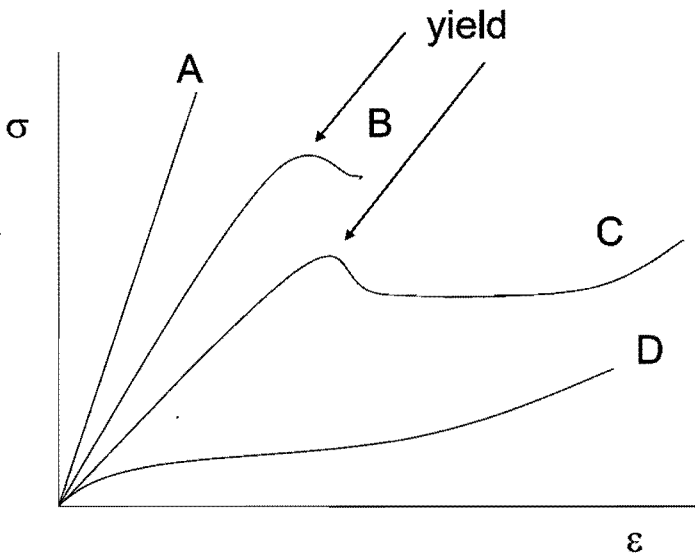


Figure 2.5. Different types of behaviour during tension: elastic (A), plastic (B, C), and rubber-type elastic (D).

Another important difference can be seen when you observe the behaviour of materials during first stretching and then relaxing again. As depicted in Figure 2.6, materials can be *completely or linearly elastic* (A) like ceramics; *elastic–plastic*, where a part of the deformation is reversible (B), like most metals; *completely plastic* (C) as polymers can be; and *visco-elastic*, where the deformation is completely reversible, but the curves are not the same for tension and release (D). During this latter process energy is lost. In general this last type of behaviour is called **hysteresis**.

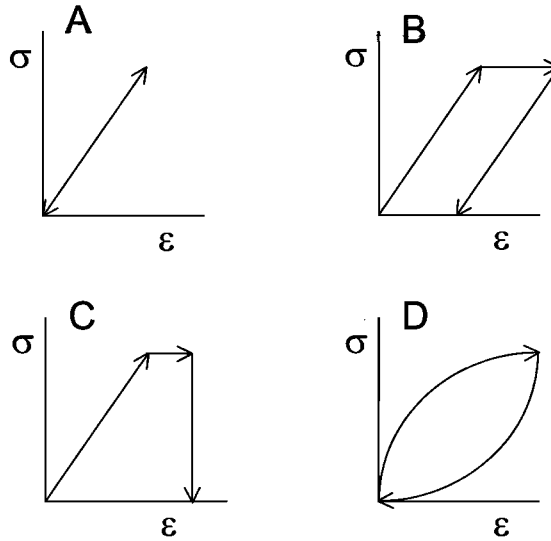


Figure 2.6. Different types of behaviour during a tensile test where force is first applied and then removed: completely reversible (A), partly irreversible (B), completely irreversible, and reversible with loss of energy (D).

When a metal or polymer undergoes a tensile test, it will first show elastic stretching, and then yield and plastic deformation. It does not start flowing like a liquid: the stress still rises, so the material continues to resist deformation. This is called **strain hardening** or **work hardening**, and the cause for it will be explained in Chapter 8.

However, at a certain strain, a maximum stress is reached: the (ultimate) **tensile strength** (σ_T , see Figure 2.7). Usually, the material can be stretched a bit further, until it breaks, at the breaking strength and the **maximum strain** (ϵ_{\max}). It may seem strange that the material breaks at a lower stress than the tensile stress, but this is an artefact of our definitions, as will be explained in the next section.

The length of the (two combined pieces of the) material after breaking is used to calculate the **ductility**:

$$\frac{L_{\text{final}} - L_0}{L_0} \quad (\text{often in \% , so then multiply with 100})$$

Also, the reduction in cross-sectional area is used to indicate ductility:

$$\frac{A_0 - A_{\text{final}}}{A_0}$$

This is easily related to the change in length when $\Delta V = 0$.

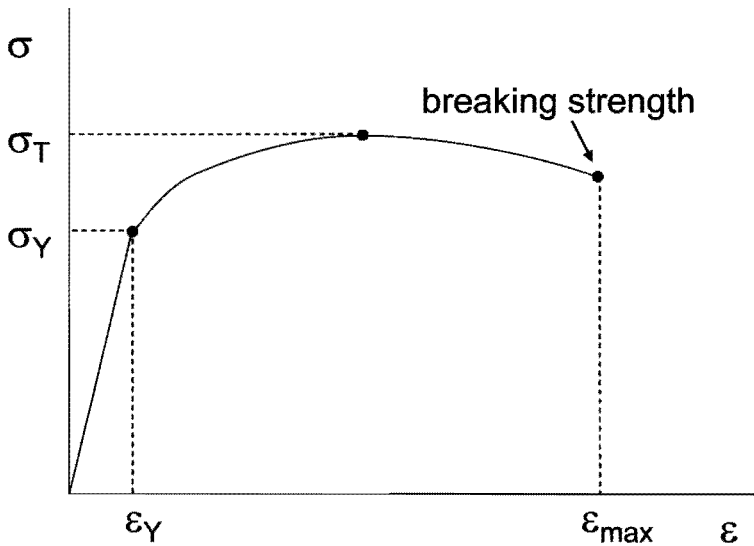
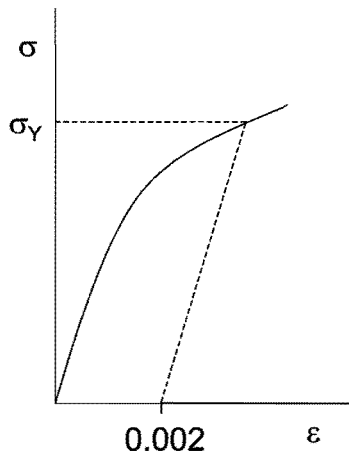


Figure 2.7. A tensile test for a material showing yield.

Intermezzo

Usually the transition from elastic to plastic behaviour is not very clear. Often, the yield point is then defined as the 0.2% offset yield: a line is drawn parallel to the linear part of the curve, starting at $\varepsilon = 0.002$. The intercept with the curve is then defined as the yield point.



Since there may be some elastic **recovery** after breaking (elastic–plastic behaviour), the ductility can be smaller than expected from ε_{\max} . In Figure 2.8, $\sigma_{Y,1}$ is the yield stress at the first elongation. At higher stresses there is plastic deformation, and after release of the stress elastic strain recovery is seen. The double-headed arrow

indicates the recovery, but the material stays permanently elongated. $\sigma_{Y,2}$ is the higher yield stress when the material is stretched a second time.

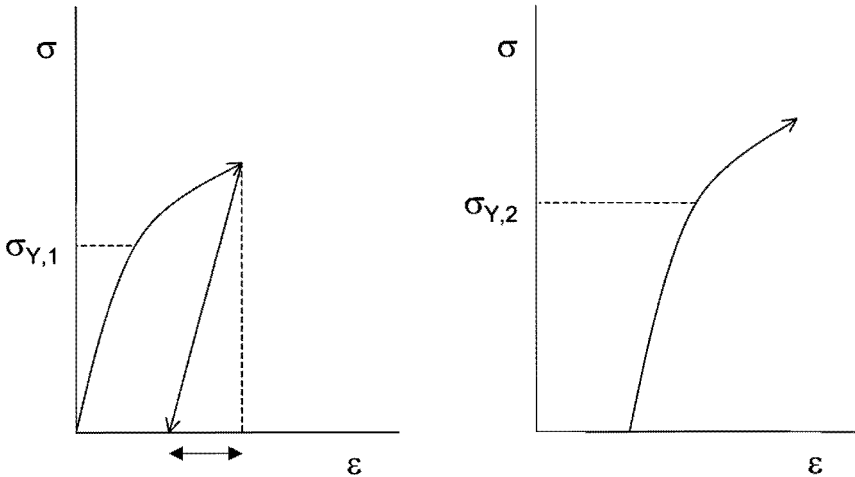


Figure 2.8. Elastic recovery may not be complete, giving a higher yield stress in the next tensile test.

The total area under the stress–strain curve is again energy per m^3 (compare with the elastic energy): it is the total energy necessary for breaking the material. This is usually called the **toughness** of the material. Of course, if the ductility is high, so will be the toughness.

There are some remarks we must make about fracture, because there are two quite different kinds of fracture (see Figure 2.9). Ceramics will usually show **brittle fracture**: this is a very fast process at the end of the elastic region. Metals usually show **ductile fracture**, as seen in the tensile test: a slower process that involves necking at σ_T (see section 2.3) and plastic deformation. However, metals can also undergo the faster brittle fracture at any point of the tensile test, especially at lower temperatures. Which kind of fracture occurs first for metals will be investigated in Chapter 5.

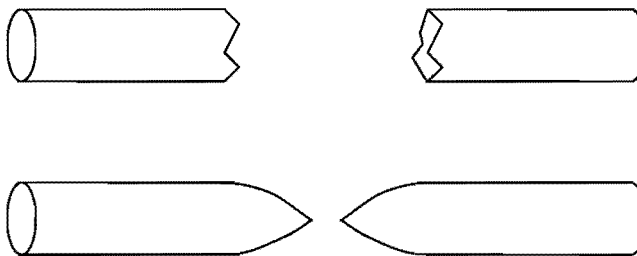


Figure 2.9. Brittle fracture (top) vs. ductile fracture (bottom).

Where in the stress–strain curve can we find the various mechanical properties? This is demonstrated in Figure 2.10.

Stiff materials have a high slope in the elastic region (high E), while **flexible** or compliant or pliant materials have a low E .

Brittle materials have a large resistance to plastic deformation (high σ_Y), while **ductile** materials can be deformed easily (low σ_Y).

Strong materials have a high tensile strength (σ_T), while **weak** materials have a low σ_T . However, some people call a material weak when it shows yield at low stresses (low σ_Y). Of course, when the material does not show yield (such as ceramics), the strength is determined by the end of the elastic region.

A **tough** material can absorb a lot of energy before breaking (large area under the curve): it usually can be deformed a lot (high ϵ_{\max}). If the area is small, the material is brittle.

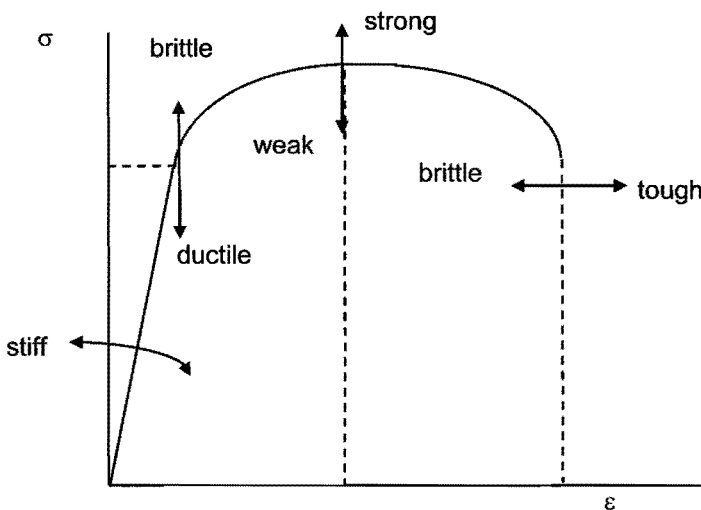


Figure 2.10. The various mechanical properties in the stress–strain curve.

A property that is often mentioned, and that can be very easily measured, is the **hardness** of a material. It represents the resistance to local plastic deformation, such as scratching or indentation. It is defined purely empirically, and can not be easily related to the properties above. For metals, it is related to the tensile strength, and also to the yield stress. For non-metals, it is related to the lattice energy: the strength of the chemical bonds. For these materials, it is also related to the yield strength in compression. We will not discuss it in more detail.

2.3 True stress and strain

In the stress–strain curve of metals, we saw a strange behaviour for ductile fracture: there is a maximum stress (σ_T), but the material breaks at a lower stress and a higher strain. How can this happen?

The cause is our definition of stress, which is related to the original cross-sectional area. This is called the **engineering stress**:

$$\sigma = \frac{F}{A_0}$$

This is not the actual stress in the material, because the area of the cross-section will usually decrease during the tensile test (or increase during compression). We therefore must look at the **true stress**:

$$\sigma_t = \frac{F}{A}$$

If we now assume that the volume does not change during tension, then we can say: $A/A_0 = L_0/L$, and this leads to:

$$A = \frac{A_0}{1 + \epsilon}$$

The relation between true and engineering stress is then:

$$\sigma_t = \sigma \frac{A_0}{A} = \sigma(1 + \epsilon)$$

For small values of ϵ , σ_t and σ are approximately equal.

However, at the maximum engineering stress, the material shows **necking**; at one location, the area A suddenly becomes smaller very rapidly (see Figure 2.11). The true stress (σ_t) still increases after this point, but since the area (A) decreases faster than the true stress increases, the engineering stress (σ) goes down:

$$\sigma = \sigma_t \frac{A}{A_0}$$

For more details, see Appendix B.

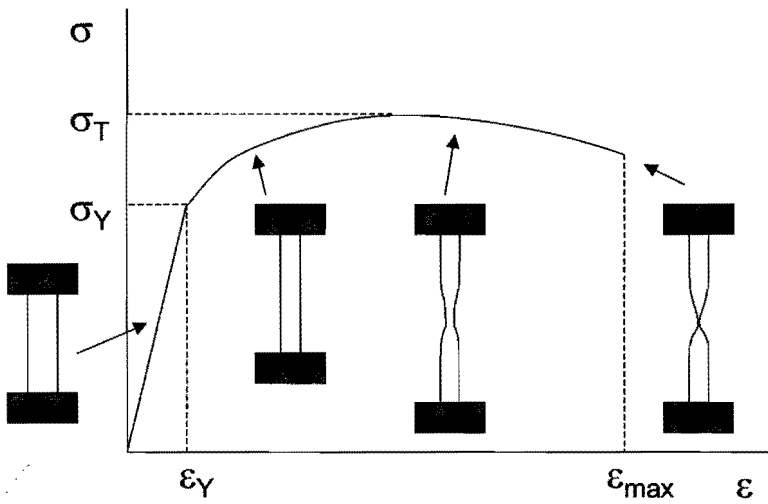


Figure 2.11. Necking occurs at the tensile stress, leading quickly to ductile fracture.

In Figure 2.12 we see the engineering stress (solid line) and the true stress (dashed line) for a tensile test:

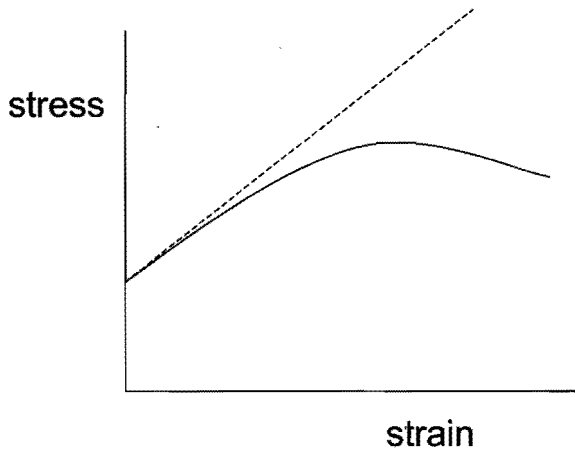


Figure 2.12. True stress keeps on increasing (dashed line), even when the engineering stress goes through a maximum (solid line).

In order to describe the behaviour of the true stress before the necking, it is also necessary to use another measure for the strain, the true strain:

$$\epsilon_t = \int_{L_0}^L \frac{dL}{L} = \ln\left(\frac{L}{L_0}\right) = \ln(1 + \epsilon) \quad \epsilon = (e^{\epsilon_t}) - 1 \Rightarrow \text{engineering neck}$$

While the **engineering strain** ϵ runs from -1 to $+\infty$, ϵ_t has a more symmetrical range from $-\infty$ to $+\infty$. In Figure 2.13, ϵ_t is plotted as a function of ϵ . For small values of ϵ , ϵ and ϵ_t are approximately equal.

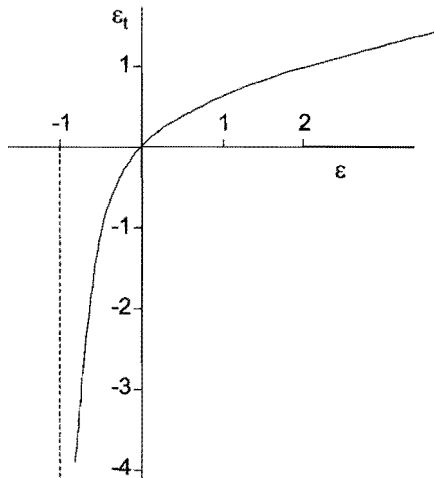


Figure 2.13. Relation between true strain and engineering strain.

We can now describe what happens during the tensile test.

1. In the *elastic* region: $\sigma = E\epsilon$, and also: $\sigma_t = E\epsilon_t$, until yield: $\epsilon = \epsilon_t = \epsilon_Y$.
2. In the *plastic* region it is found that there is a simple, empirical relation between true stress and true strain:

$$\sigma_t = K_{pl} \epsilon_t^N$$

- 1) basic relationship
- 2) stress vs true strain is N
- 3) engineering neck $\epsilon = e^{\epsilon_t} - 1$

K_{pl} and N are material properties; N is called the strain hardening exponent.

It can now be shown (see Appendix B) that necking occurs when the true strain equals the exponent N :

$$\epsilon_t = N \quad \text{true strain}$$

3. After the necking the true stress still increases, but this is very difficult to describe, since the necking will quickly lead to ductile fracture.

Example: A material yields at an engineering strain $\epsilon_Y = 0.002$, has a Young's modulus $E = 1$ GPa, and $N = 0.1$. Necking will then occur at $\epsilon_t = 0.1$, or $\epsilon = 0.11$. In the elastic region we have $\sigma = E\epsilon$, and $\sigma_t = E\epsilon_t$. At the yield point we must have: $\sigma_Y = E\epsilon_Y = 0.002$ GPa. σ_t and ϵ_t are approximately the same as σ and ϵ at this point.

2.4 Overview of material properties

In Figures 2.16 and 2.17, a graphical overview is given of some typical ranges for the mechanical properties of several types of materials. We will see in Chapter 5 why normalized yield stress and normalized toughness are used.

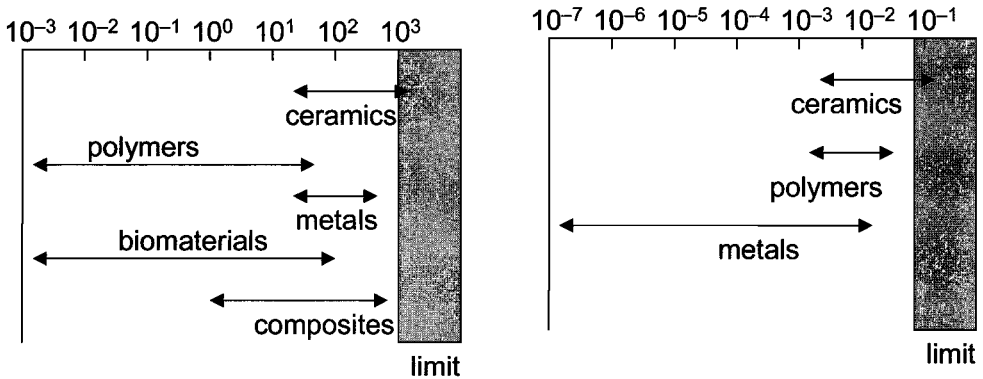


Figure 2.16. Left: Young's modulus (E [GPa]); right: normalized yield stress (σ_Y/E).

For a lot of applications, materials have to be heated—for processing, shaping, or sterilizing—and the melting temperature (in kelvin) can be very important.

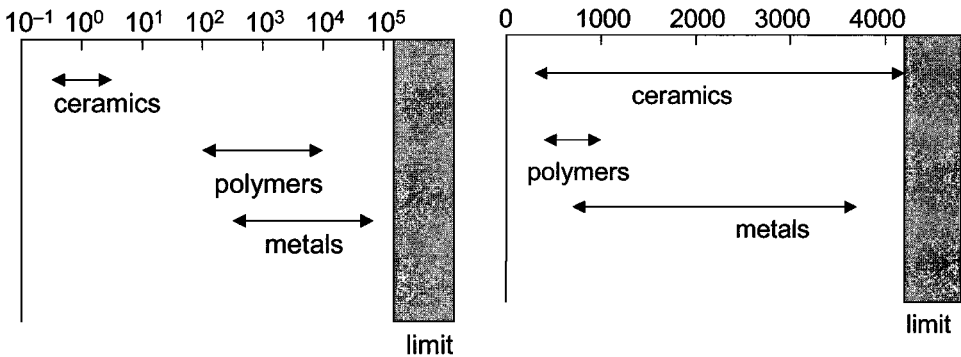


Figure 2.17. Left: normalized toughness; right: melting temperature [K].

There are various other graphical methods to quickly compare different materials, where e.g. stiffness (E) and weight (ρ) can be compared, or strength (σ_T) and weight (ρ). Also, the three properties can be combined in a diagram of reduced strength (σ_T/ρ) vs. reduced stiffness (E/ρ). These diagrams can be found in various books, and are very useful for selecting materials.

Problems

- 2.1.a. What is the final length of a 2 m long cylindrical bar of copper, 0.01 m in diameter, stressed by a 5 kN force?
- b. If a steel bar of the same diameter has the same force applied to it, how long must it be initially to extend the same amount as the copper bar in a.?
- 2.2. A specimen of Al with a rectangular cross section (10 mm x 12.7 mm) is pulled in tension with 35.5 kN, producing only elastic deformation. Calculate the resulting strain.
- 2.3. A cylindrical Ti implant with diameter 19 mm and length 200 mm is deformed elastically in tension with a force of 48.8 kN.
- a. Calculate the elongation.
- b. Calculate the change in diameter.
- 2.4. A steel pipe is hanging vertically down from a support. The pipe has an outer diameter of 7.5 cm, an inner diameter of 5 cm, a density of 7.90 Mg/m^3 , and a yield strength of 900 MPa. Assume a safety factor of 2.
- a. What is the maximum length of the pipe before yield occurs?
- b. What is the maximum elastic strain in the pipe, and at what location along the pipe does it occur?
- c. At what location along the pipe does the elastic strain have a minimum value?
- 2.5. The engineering stress–strain curve for a given implant metal can be described by three straight lines, with σ in MPa.
- Elastic: $\sigma = 138000\varepsilon$ for $0 < \varepsilon < 0.0025$
- Plastic: $\sigma = 327 + 7075\varepsilon$ for $0.0025 < \varepsilon < 0.1$
- and: $\sigma = 1725 - 6900\varepsilon$ for $0.1 < \varepsilon < 0.15$
- a. What is the value of Young's modulus?
- b. What is the value of the yield stress?
- c. What is the value of the ultimate tensile stress?
- d. Calculate a value for the resilience.
- e. Calculate a value for the toughness.
- f. What is the percentage elongation?

2.6. A specimen of ductile cast iron with a rectangular cross section (4.8 mm × 15.9 mm) is deformed in tension. The results are given below.

Load/N	Length/mm
0	75.000
4310	75.025
8610	75.050
12920	75.075
16540	75.113
18300	75.150
20170	75.225
22900	75.375
25070	75.525
26800	75.750
28640	76.500
30240	78.000
31100	79.500
31280	81.000
30820	82.500
29180	84.000
27190	85.500
24140	87.000
18970	88.725

fracture

Determine the following properties:

- The modulus of elasticity.
- The tensile strength.
- The resilience.
- The ductility in percent elongation.

2.7. A tensile bar has a circular cross section of area 0.2 cm^2 . The applied loads and corresponding lengths recorded in a tensile test are:

Load/N	Length/cm
0	2.0000
6000	2.0017
12000	2.0034
15000	2.0042
18000	2.0088
21000	2.043
24000	2.30
25000	2.55
22000	3.00
	fracture

After fracture the bar diameter was 0.37 cm .

Determine the following:

- Young's modulus.
- Ultimate tensile stress.
- Percentage reduction of area.
- True fracture stress.

2.8. For a hardened steel alloy the true stress–strain behaviour is:

$$\sigma_t = 1310 \varepsilon_t^{0.3} \text{ [MPa]}$$

- What is the true strain at necking?
- What is the engineering strain at necking?
- What are the true and engineering stress levels at necking?

2.9. A tensile test is performed on a metal specimen, and it is found that a true plastic strain of 0.20 is produced when a true stress of 575 MPa is applied; for this metal, the value of K_{pl} is 860 MPa .

- Calculate the true strain that results from a true stress of 600 MPa .
- Calculate for both true strains the corresponding engineering strains and stresses.

2.10. Wire used by orthodontists to straighten teeth should ideally have a low modulus of elasticity and a high yield stress. Why?

2.11.* A cylindrical stainless steel wire must be implanted. The steel has a Young's modulus of 193 GPa , and yields at $\varepsilon = 0.0015$.

- How large must the diameter of the wire be to show no plastic deformation at a load of 900 N ?

If there is yield at higher loads, we want to prevent necking, since this will lead to fracture and damage for the surrounding tissue. For the plastic deformation of this steel it is known that: $K_{pl} = 1275 \text{ MPa}$ and $n = 0.45$.

- Calculate the force where necking occurs for this wire. Clearly indicate all assumptions.

3 Bonds between atoms:

Microscopic structure and elastic modulus

There are several types of bonds that can keep materials together (see Chapter 1), but most of them can be modelled in a simple way as a combination of attraction and repulsion terms.

Elastic deformation occurs through the stretching or compression of bonds between atoms, so in principle we can calculate the Young's modulus E of a material if we know how the bonds behave. This is the only mechanical property we can calculate from the microscale structure.

Live as if you were to die tomorrow; learn as if you were to live forever.

Mohandas Karamchand "Mahatma" Gandhi
(1869–1948)

3.1 Bond energy

All bonds have an *attraction* between atoms due the chemical bonding, which lowers the energy, and a *repulsion* between atoms due to the repulsion between the positively charged nuclei, which prevents atoms from coming too close.

A formula that is used a lot to describe the energy in such a case is:

$$U = -\frac{A}{R^m} + \frac{B}{R^n} \text{ [J]}$$

Here, A and m represent the attractive term, and B and n represent the repulsion. It is mostly found that $n = 12$. For van der Waals forces $m = 6$ is often used, and for forces between dipoles $m = 3$. The interatomic distance R is the sum of the two atomic (or ionic) radii. The relation between energy and distance can be seen in Figure 3.1.

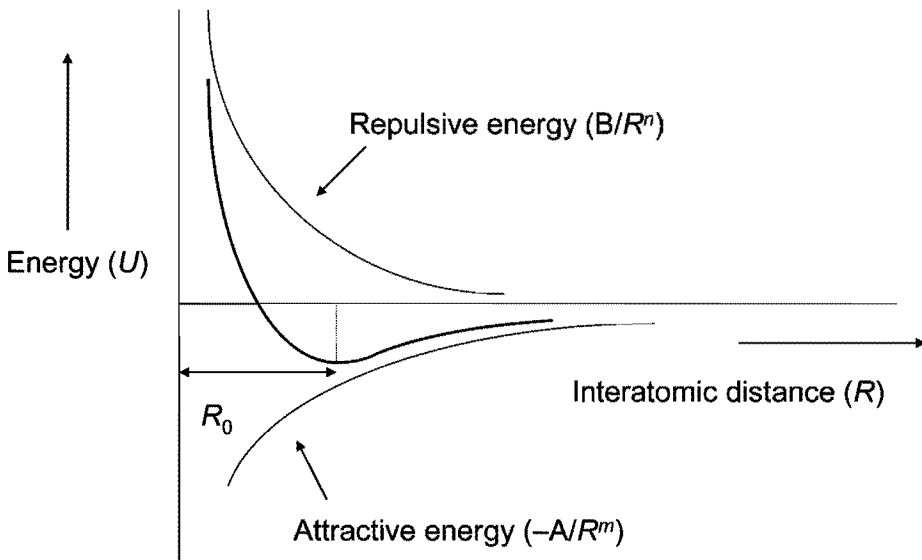


Figure 3.1. The energy in a bond between two atoms or ions is built up from an attractive and a repulsive term.

For electrostatic forces, which are important in salts, the attraction term is given by Coulomb's law for two charges (q_1 and q_2), separated by a distance R :

$$U = \frac{q_1 q_2}{4\pi\epsilon_0 R} \text{ [J]}$$

So, for the attraction energy of ions in salts we have $m = 1$, and, by writing q_1 and q_2 as multiples of the unit charge e ($q_1 = z_+e$ for the cation and $q_2 = z_-e$ for the anion), we get:

$$A = -\frac{z_+z_-e^2}{4\pi\epsilon_0} = -2.3 \cdot 10^{-28} z_+z_- [\text{Nm}^2]$$

Therefore the total energy between ions in salts can be written as:

$$U = \frac{z_+z_-e^2}{4\pi\epsilon_0 R} + \frac{B}{R^n} \text{ [J]}$$

Two atoms form a stable bond at the distance where the energy U is minimal, so when:

$$\frac{dU}{dR} = 0$$

Using the general formula for U , this leads to an interatomic distance:

$$R_0 = \left(\frac{nB}{mA} \right)^{1/(n-m)} \text{ [m]}$$

With this relationship, one can later on always eliminate B from all formulas via:

$$B = \frac{mA}{n} R_0^{n-m}$$

which is often useful.

The energy at the equilibrium distance R_0 is now defined as:

$$U_0 = U(R_0)$$

For electrostatic bonds in salts, where $m = 1$, elimination of B leads to a simple formula for the equilibrium energy for two atoms (check this!):

$$U_0 = -\frac{A}{R_0} \left(1 - \frac{1}{n} \right) \text{ [J]}$$

Intermezzo

In real materials, there are of course more than two ions present. Some ions are oppositely charged, and others have the same charge. Also, not all ions are at the same distance from each other. If you average the effect of all other ions surrounding one ion, the formula for the attractive energy is not that different from the one we derived:

$$U = \frac{N_A A z_+ z_- e^2}{4\pi\epsilon_0 R} \text{ [J/mol]}$$

The only difference is the so-called Madelung constant A , which is different for each salt. E.g. for NaCl: $A = 1.7476$, and for CsCl: $A = 1.7627$.

This constant is obtained by adding the electrostatic contributions from ions at different distances: e.g., the closest 6 are attractive, the next 12 are repulsive, the next 8 are attractive again...

$$A = 6 - 12 \times 1/\sqrt{2} + 8 \times 1/\sqrt{3} - \dots$$

To understand these numbers, you should take a look at Chapter 4 on crystal structures.

The repulsive force is then introduced in the so-called Born–Landé equation exactly as we have done:

$$U = \frac{N_A A z_+ z_- e^2}{4\pi\epsilon_0 R} \left(1 - \frac{1}{n} \right) \text{ [J/mol]}$$

The n in this equation is also dependent on the ions involved. It is the average of the values for the ions from the list:

n	ion
5	H ⁻ , Li ⁺
7	F ⁻ , O ²⁻ , Na ⁺ , Mg ²⁺
9	Cl ⁻ , S ²⁻ , K ⁺ , Ca ²⁺ , Cu ⁺
10	Br ⁻ , Rb ⁺ , Sr ²⁺ , Ag ⁺
12	I ⁻ , Cs ⁺ , Ba ²⁺ , Au ⁺

As you can see, n is related to the size of the ions.

The simple theory for 2 ions is therefore quite good.

3.2 Forces on bonds

The *force* between the atoms can be easily calculated from the energy curve in the usual way:

$$F_a = -\frac{dU}{dR} = -\frac{mA}{R^{m+1}} + \frac{nB}{R^{n+1}}$$

In Figure 3.2, we can see the force *between* the atoms. A positive force here means repulsion, so the atoms want to move apart, and a negative force means attraction, so the atoms want to move closer together. The force is exactly zero at the equilibrium distance, as it should be.

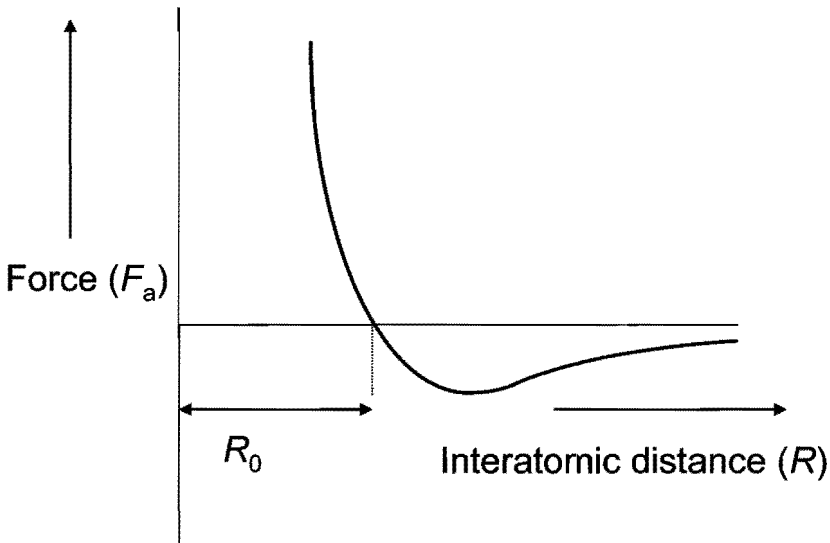


Figure 3.2. The dependence of interatomic forces on the distance.

Usually, we are interested in the force we need to deform a material from the *outside*, so we use the formula with an inverted sign:

$$F = \frac{dU}{dR} = \frac{mA}{R^{m+1}} - \frac{nB}{R^{n+1}}$$

Now we have the usual behaviour as seen in Chapter 2: a negative force is needed to compress the material (atoms closer together), and a positive force is necessary to stretch the material (atoms further apart). This is illustrated in Figure 3.3.

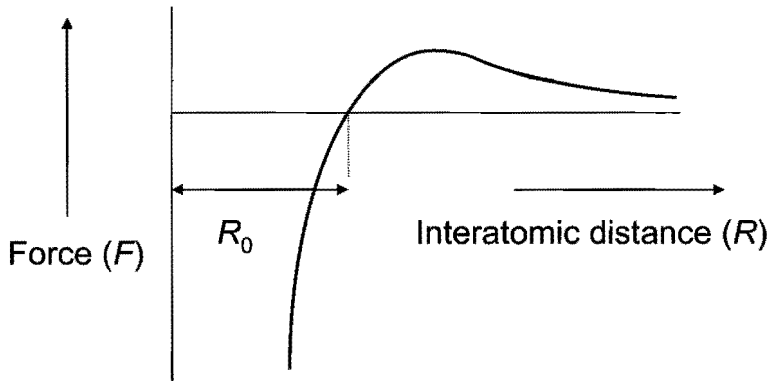


Figure 3.3. The force needed externally to change the distance between the atoms.

For elastic behaviour, we are interested what the resistance is against small changes in the bond length between the atoms. *Only* for very small deformations, we can *approximate* this as the behaviour of a spring by drawing a straight line:

$$F = k_s(R - R_0)$$

The spring constant k_s can be calculated from the slope of the F, r -curve at $R = R_0$:

$$k_s = \left(\frac{dF}{dR} \right)_{R=R_0} = -\frac{m(m+1)A}{R_0^{m+2}} + \frac{n(n+1)B}{R_0^{n+2}}$$

This looks quite complicated, but with the relation we saw earlier for R_0 , we can write $B = (mA/n)R_0^{n-m}$, and then we get:

$$k_s = \frac{m(n-m)A}{R_0^{m+2}}$$

We can now relate this spring constant k_s for two atoms to the Young's modulus E of the material by realizing that the strain here is:

$$\varepsilon = \frac{R - R_0}{R_0}$$

Since the atoms have distance R_0 , this is also roughly their diameter, and they therefore use an area of about R_0^2 , the stress is:

$$\sigma = \frac{F}{R_0^2}$$

With $F = k_s(R - R_0)$, we then get:

$$E = \frac{\sigma}{\varepsilon} = \frac{k_s}{R_0} = \frac{m(n-m)A}{R_0^{m+3}}$$

m = 1 van der Waals

This very rough approximation gives reasonable predictions for the Young's modulus. Of course, we can perform more realistic calculations when we know more about the bonds.

Example: For salts we know that $m = 1$, and that $A = -2.3 \cdot 10^{-28} z_+ z_-$ for ions of charges z_+ and z_- . If we then know the values of n and R_0 , we can calculate E . For NaCl, it is known that $R_0 = 0.282$ nm, and that $n = 9.4$. Also, the ions have charges $+1$ and -1 . This leads to the prediction: $E = 305$ GPa. Experimentally it is found that: $E = 49$ GPa, so we are only a factor 6 off.

3.3 General characteristics

Metals: The metallic bond is quite strong (cohesive energy: 100–800 kJ/mol), and is isotropic: it has the same strength in all directions ("electron sea"). We will show in Chapter 5 that this leads to the easy deformation of metals. The predicted Young's moduli are 60–300 GPa, and this fits quite well with experimental values.

Ceramics: The bonds are very strong (ionic: 600–1500 kJ/mol, or covalent: 300–700 kJ/mol), but **anisotropic**: they depend on the location of the nearby atoms. We will see in Chapter 5 that this leads to the brittleness of these materials. This holds especially for covalent networks, where the bonds are located exactly between pairs of atoms. In ionic bonds, the bonds are directed between the $+$ and $-$ charges on the cations and anions. For covalent bonds a Young's modulus of 200–1000 GPa is predicted, and for ionic bonds: 32–96 GPa. These values fit quite well with experimental values, although for ionic ceramics they are on the low side.

Polymers: Bonds between macromolecules are quite weak (van der Waals, H-bonds: 10–50 kJ/mol). The predicted values for the Young's moduli are 8–12 GPa (H-bonds) and 2–4 GPa (van der Waals), but many polymers have much lower moduli. This is due to the fact that most polymers are in fact not completely solid, but partly molten ("liquids in slow motion"). We will discuss this in more detail in Chapters 6 and 7.

Problems

3.1. A common form for the potential energy of interaction between atoms is given by $U = -A/R^6 + B/R^{12}$, where A and B are constants.

- Derive an expression for the equilibrium distance between the atoms in terms of A and B.
- If $R_0 = 0.25$ nm, what is the ratio of B to A?
- Derive an expression for the energy at the equilibrium separation distance in terms of A.

3.2. The ionic solids LiF and NaBr have the same structure as NaCl. For LiF, $n = 5.9$ and $R_0 = 0.201$ nm, whereas for NaBr, $n = 9.5$ and $R_0 = 0.298$ nm.

- Which of these materials is expected to have the highest modulus of elasticity?
- Calculate the molar energy of ionic interactions for both materials. $U(R_0)$ J/mol

3.3.a. Opposite sides of a rock salt (NaCl, with $n = 9.4$) crystal are pulled to extend the distance between neighbouring ions from $R_0 = 0.2820$ nm to $R = 0.2821$ nm. Similarly, during compression, ions are squeezed to a distance of 0.2819 nm. Compare the value of the tensile (or extension) force with that of the compressive force. Are they the same?

- Repeat the calculation if the final distances are 0.2920 nm for extension and 0.2720 nm in compression.

3.4. The potential energy U between two ions is sometimes represented by:

$$U = -\frac{C}{R} + De^{-R/\rho}$$

- Derive an expression for the bond energy U_0 in terms of the equilibrium separation R_0 and the constants D and ρ .
- Derive an expression for U_0 in terms of R_0 , C , and ρ .

3.5.* We can treat zirconia (ZrO_2) as an ionic ceramic with a rock salt structure, consisting of Zr^{4+} and O^{2-} ions. Calculate the exponent n of the repulsion term in the interaction energy between the ions from the Young's modulus.

$$r(Zr^{4+}) = 0,087 \text{ nm}$$

$$r(O^{2-}) = 0,132 \text{ nm}$$

4 Inorganic Materials I: Structure of crystalline metals and ceramics, and glasses

Metals and ceramics are among the most important “strong” construction materials, in contrast to the “soft” polymers. They are used a lot as engineering materials, but also as biomaterials.

Inorganic materials are mostly crystalline, so in this Chapter we will first focus on the structure of crystalline materials, and we will take a short look at non-crystalline glasses.

In the next Chapter we will see what the implications of these structures are for the mechanical properties of inorganic materials.

It is not by prayer and humility that you cause things to go as you wish,
but by acquiring knowledge of natural laws.

Bertrand Russell
(1872–1970)

4.1 Introduction

In inorganic materials, the bonds are ionic, covalent or metallic, and the structures are mostly **crystalline**. Such structures are highly symmetric, and can be described by repetition of a unit cell. Deformation of these materials is mainly determined by the bonds between the atoms and by imperfections in the crystal structure. When a crystalline substance loses its order, we call it a **glass**.

4.1.1 Bioceramics

In the human body we do not find metals as natural materials, and almost no pure ceramics. Most ceramics are present as part of a composite material, such as bone or tooth (see Chapter 9). In these composites, a large control is seen in the way the ceramics are formed, guided by organic polymers. Because biological composites are formed by growth, the formation of the crystals can be tuned exactly in time and structure (**biomineralization**).

The minerals most often found as bioceramics are calcium carbonate (CaCO_3), hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$), and silica (SiO_2). Only hydroxyapatite is found in the human body. CaCO_3 normally forms calcite crystals, but a number of organisms can change the crystal growth completely for their own purposes. Also, SiO_2 is used for many beautiful structures, such as in diatoms.

Intermezzo

Biomineralization is also called "molecular tectonics": the building of structures with molecules. This process has a number of stages:

- The organic molecules organize themselves, e.g. as polymer networks or vesicles.
- There is recognition between charged groups on the organic surface and the inorganic ions. This is determined by the location and nature of the charged organic groups.
- The morphology (shape) of the growing crystal is now directed: some planes of the crystal can grow, and others not, by adsorption of organic molecules.
- Various small crystals are organized in larger structures.

For more information: S. Mann, Biomimetic materials chemistry.

4.1.2 Inorganic biomaterials

Metals that are used a lot as biomaterial are: titanium, stainless steel (Fe with C, Cr, Ni, Mo, Cu), cobalt/chromium alloys (e.g. Vitallium: Co_2Cr with Ni and Fe), and gold. They are used a lot as replacements for joints, plates and screws in bone, and root implants in teeth.

Metals are often strong and tough, but they have a high density and can corrode in a biological environment. A typical biomedical application is amalgam for fillings: an alloy of 60% Ag, 29% Sn, 6% Cu, 2% Zn and 3% Hg is dissolved in mercury. Then, the Ag_3Sn starts to react with Hg, and Sn_7Hg and Ag_2Hg_3 are formed. The final solid has the composition: 45–55% Hg, 35–45% Ag, and 15% Sn.

Ceramics that are used a lot as biomaterial are alumina (polycrystalline Al_2O_3 ; hip prosthesis, tooth components), zirconia (ZrO_2 , orthopaedic and dental applications), hydroxyapatite (bone and tooth replacement) and carbon (heart valves, ligaments,

dentistry). Ceramics are often inert, biocompatible and strong in compression, but they are also brittle and hard to shape.

Glasses are employed in orthopaedic applications and as bone replacements. Also the glass-ceramics are used, such as Macor, which has mica crystals mixed with a glass consisting of SiO_2 , B_2O_3 , Al_2O_3 , MgO , K_2O and F^- . Then there are the bioactive glasses, which can integrate with bone, such as Bioglass (CaO , P_2O_5 , Na_2O , and SiO_2).

Drugs can also sometimes be offered better as glasses than as crystalline powders, because they will then dissolve more quickly. This happens because the glassy state is less stable than the crystalline state (see section 4.6).

Intermezzo

"Bioceramics": Gems, worn on the human body

- Corundum (Al_2O_3): colourless crystals. With Cr added: red rubies. With Fe and Ti added: blue sapphires.
- Quartz (SiO_2): colourless crystals. With FeO added: purple amethysts. With MgO and FeO added: brown-red layers in agate. Amorphous SiO_2 : milky white opal.
- Beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$): hexagonal crystals. With Cr added: green emeralds.
- Diamond (C): cubic crystals.

The well-known vibrations given off by crystals and their effect on human health are not treated here. ☺

Also, the healing magnetic fields of metals are ignored. ☺☺

4.2 Crystal lattices

When we want to describe the structure of a crystalline substance, we must specify the **unit cell**, and the atoms in it. The unit cell is the repeating unit in the pattern of atoms in the **crystal**. For simplicity, we will first look at a repeating pattern in two dimensions (like wallpaper). As can be seen in Figure 4.1, we can find several unit cells in this **lattice**, but we usually take the smallest possible.

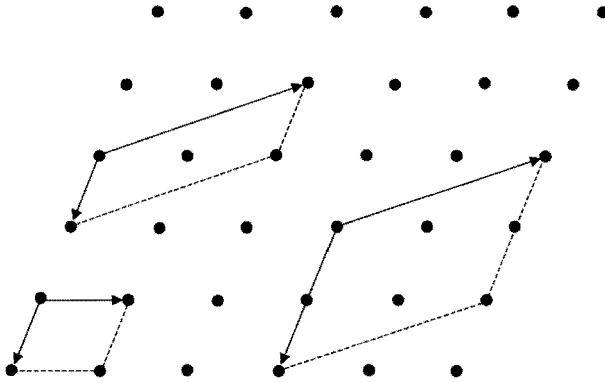


Figure 4.1. A two-dimensional lattice with several possible unit cells.

Mathematicians have been studying the symmetries of such patterns and their unit cells, and have found that there are just a few types of unit cells possible (see Figure 4.2). Usually, the following names are used: square (highest symmetry), rectangular, 120° rhombus (or hexagonal), rhombus (or centred tetragonal), and parallelogram (no symmetry).

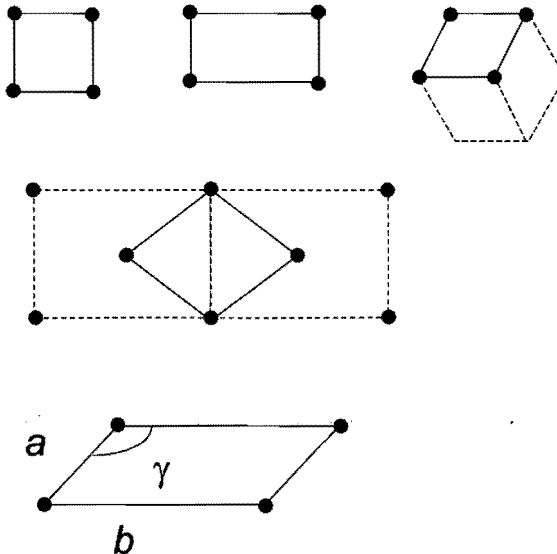


Figure 4.2. The unit cells in two dimensions that are unique.

These unit cells can be classified according to the length of their sides (a , b), the so-called **lattice parameters**, and the angle between the sides (γ), as shown in Table 4.1.

Table 4.1. The different unit cells in two dimensions.

Lattice type	$\gamma = 90^\circ$	$\gamma = 120^\circ$	$\gamma \neq 90^\circ$
$a = b$	square	hexagonal	centred rectangular
$a \neq b$	rectangular	–	parallelogram

An important trick for working with crystal lattices is counting the number of **lattice points** per unit cell: since every point on a corner belongs to 4 unit cells, it belongs for only $\frac{1}{4}$ to one cell. If there are four lattice points on the four corners, then only $4 \times \frac{1}{4} = 1$ point belongs to one cell.

Something similar can be done in three dimensions, by placing these planar lattices on top of each other. Then the following **crystal systems** are found: Figure 4.3 shows the cubic (most symmetry), tetragonal, hexagonal, and rhombohedral (or trigonal, sometimes combined with hexagonal) system, and Figure 4.4 shows the orthorhombic, monoclinic, and triclinic (least symmetry) system.

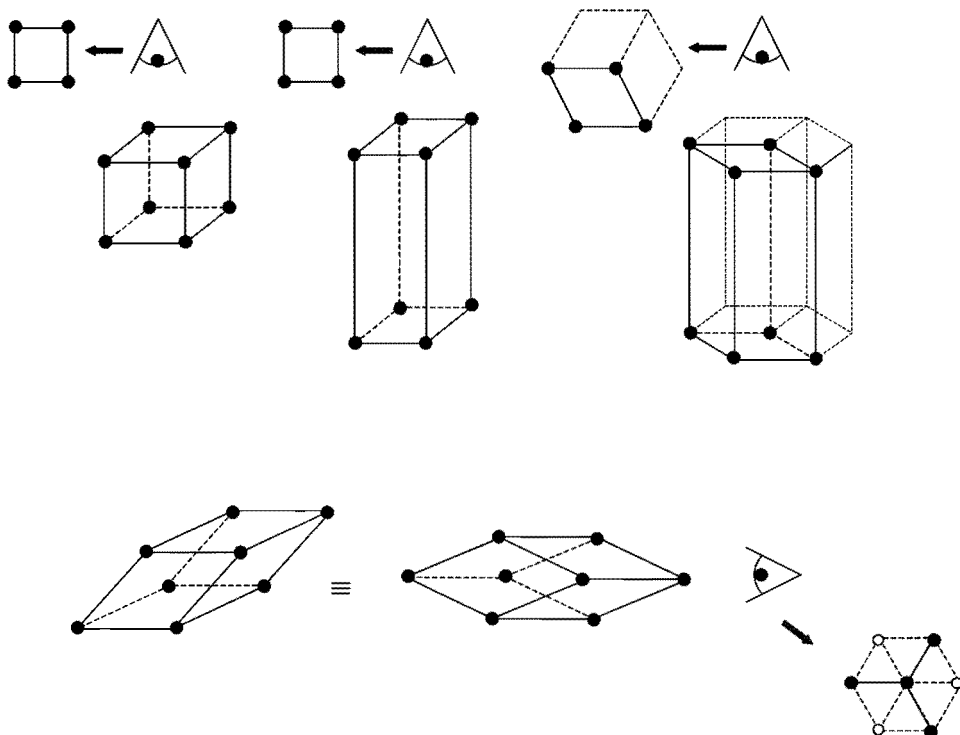


Figure 4.3. The three-dimensional unit cells with the highest symmetry. The eye symbol shows the result of a top or side view.

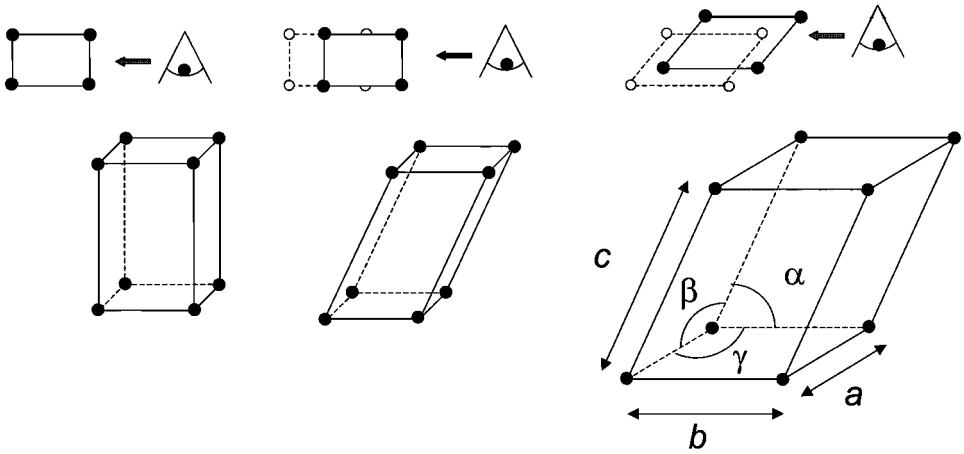


Figure 4.4. The three-dimensional unit cells with less symmetry.

These crystal systems can again be classified by the length of the sides (the lattice parameters a, b, c) and the angles between the sides (α, β, γ), as shown in Table 4.2.

Table 4.2. Classification of the three-dimensional unit cells.

Crystal system	$a = b = c$	$a = b \neq c$	$a \neq b \neq c$
$\alpha = \beta = \gamma = 90^\circ$	cubic	tetragonal	orthorhombic
$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	–	hexagonal	–
$\alpha = \beta = \gamma \neq 90^\circ$	–	–	monoclinic
$\alpha = \gamma = 90^\circ \neq \beta$	rhombohedral	–	–
$\alpha \neq \beta \neq \gamma$	–	–	triclinic

Because you get unit cells with different symmetries by placing additional lattice points on the side faces or in the centre of the unit cell, there are in total 14 **Bravais lattices** (see Figure 4.5). We will be dealing only with the **cubic** and **hexagonal structures**, since they are most often found for metals and ceramics.

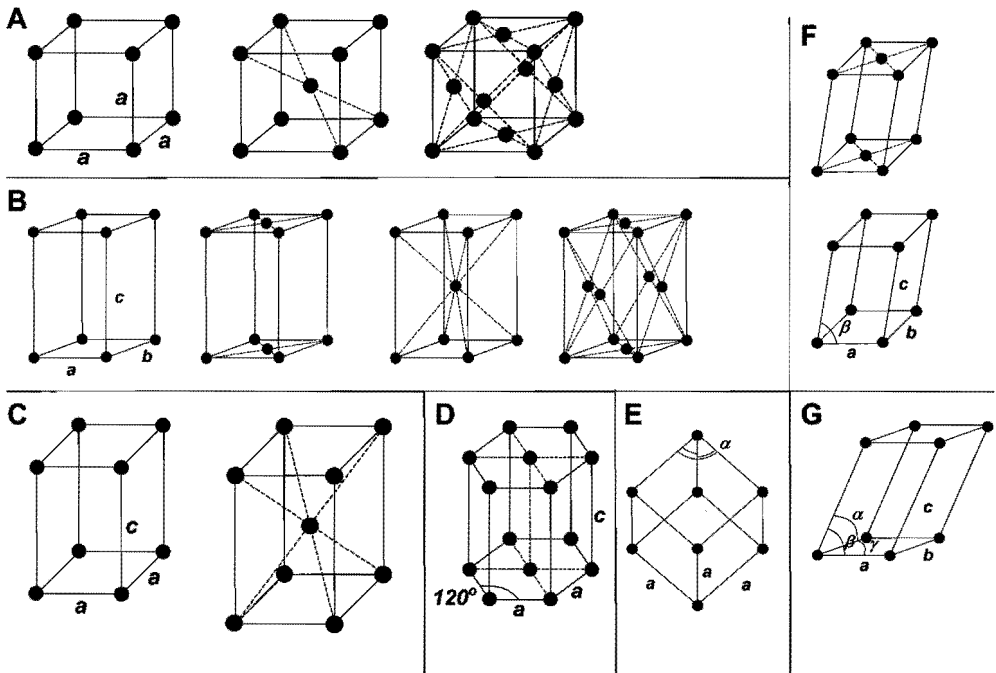


Figure 4.5. The Bravais lattices, of which three are cubic (A), four orthorhombic (B), two tetragonal (C), one hexagonal (D), one rhombohedral (E), two monoclinic (F), and one triclinic (G).

A very important point to remember is that all patterns up to now consist not of atoms, but of *mathematical points* in space. Our task is now to attach *one or more atoms* to each point, in order to make a real crystal structure. Of course, we must attach exactly the same group of atoms in the same orientation to each point, since they are mathematically identical.

4.3 Cubic and hexagonal structures

The cubic crystal system has three lattices:

- **Simple cubic (SC)**, with $8 \times \frac{1}{8} = 1$ lattice point per unit cell
- **Body-centred cubic (BCC)**, with $8 \times \frac{1}{8} + 1 = 2$ points per cell
- **Face-centred cubic (FCC)** with $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$ points per cell.

Now we must look at real materials: one or more atoms must be attached to the lattice points.

4.3.1 Cubic structures

SC: 1 atom per lattice point in an SC structure (see Figure 4.6) almost never occurs; polonium at ca. 10 °C is an example. Of course, the atoms should be touching along the edges of the cube ($a = 2r = R$); they have been drawn smaller to get a clearer picture (this is also done for the other structures). Each atom actually belongs to one unit cell for only $1/8^{\text{th}}$. Therefore each unit cell only contains 1 whole atom.

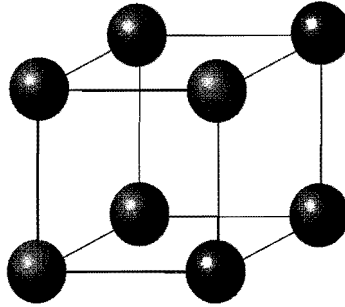


Figure 4.6. The SC unit cell with 1 atom per lattice point.

More often, 2 atoms per point is seen for SC, e.g. in caesium chloride (CsCl). This is the **CsCl-structure** (see Figure 4.7), with one atom on each lattice point, and a second (different) atom in the middle of the cube, and not on a lattice point. We still have 1 lattice point per unit cell, but now there are 2 atoms per cell. There is 1 atom of each kind per cell, so 2 atoms in total.

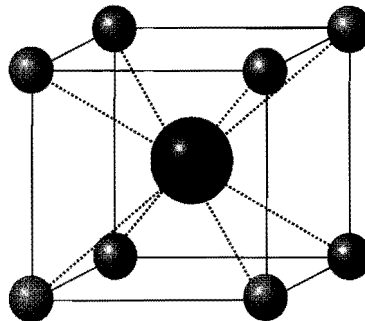


Figure 4.7. The SC unit cell with 2 different atoms per lattice point.

For **BCC** structures, 1 atom per lattice point is seen almost always for metals (Fe, Na, K, Cr, Ta, V, W), as shown in Figure 4.8. These atoms then fill about 68% of the available space in the unit cell (actually, the fraction is $\pi\sqrt{3}/8$; can you figure out why?). This looks a lot like the CsCl-structure, but now all atoms are the same. For the situation with 1 atom per lattice point, we find that the spheres touch along the so-called body-diagonal of the cube (the line between opposite corners of the cube).

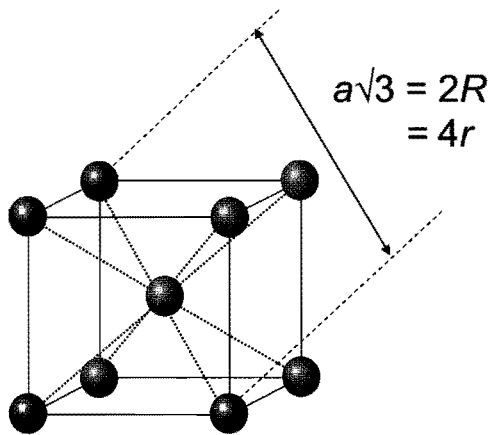


Figure 4.8. The BCC unit cell with 1 atom per lattice point.

In rare cases, we see BCC structures with more than 1 atom per lattice point (check the Table in Appendix G).

FCC structures with 1 atom per lattice point are also seen for many metals (Au, Al, Cu, Ag, Ni, Pt, Fe between 910 and 1400 °C), as shown in Figure 4.9. Here, about 74% of the available space is filled (actually, it is $\pi/(3\sqrt{2})$; why?). This is the maximum that can be obtained with spheres in a box: this is called a **close-packed structure**. In an FCC structure with 1 atom per lattice point, the atoms touch along the side diagonal of the cube.

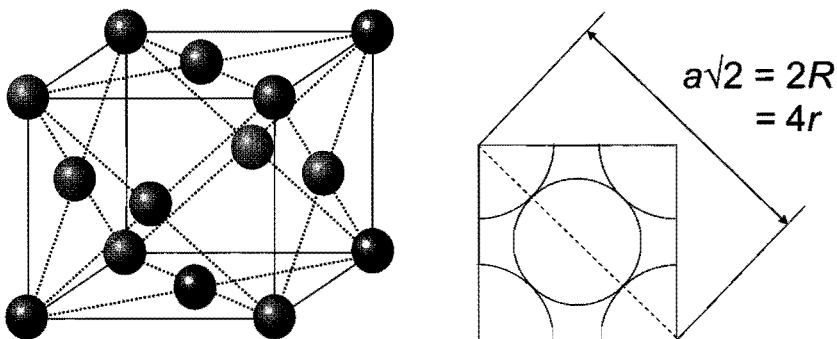


Figure 4.9. The FCC unit cell with 1 atom per lattice point.

FCC structures with 2 atoms per lattice point are seen a lot for ceramics. With 2 identical atoms per lattice point, it is called the **diamond cubic structure** (e.g. Si, Ge, C as diamond), and we get **tetrahedral structures** (Figure 4.10, left).

When the 2 atoms are different, there are several possibilities. One of them is the **zinc blende structure** (e.g. GaAs, TiC, ZnS, TiN), which is basically the same as the diamond cubic structure with different atoms (Figure 4.10, right).

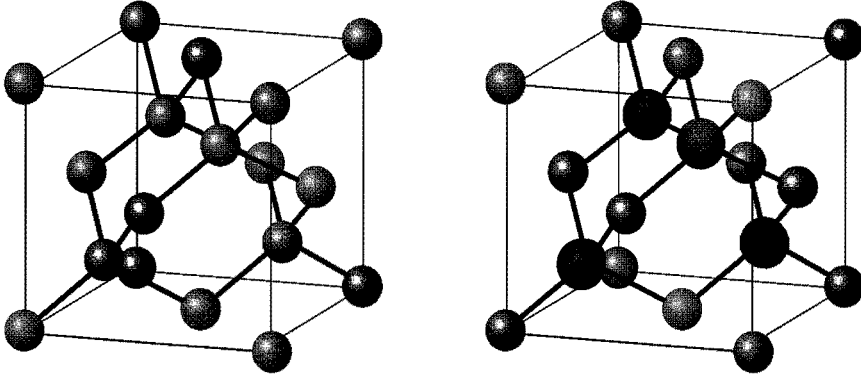


Figure 4.10. FCC unit cells with 2 identical atoms per point (left), and with 2 different atoms per point (right).

Another possibility for an FCC structure with 2 different atoms per lattice point is the **rock salt structure** (e.g. NaCl, MgO). As can be seen in Figure 4.11, this is different only in the orientation of the two-atom motif at each lattice point: it is now along the edge instead of along the body diagonal.

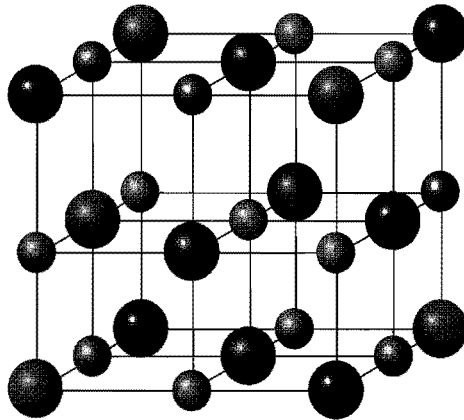


Figure 4.11. The rock salt unit cell is also an FCC cell with two different atoms per lattice point.

In the rock salt structure, the edge of the cube is related to the ionic radii as: $a = 2r_+ + 2r_-$. For ionic structures like CsCl, zinc blende, and rock salt, the relative size of the ions also determines the kind of packing (see Appendix L).

4.3.2 Hexagonal structures

Hexagonal structures are most often displayed with a hexagonal unit cell (see Figure 4.5), which contains $12 \times \frac{1}{6} + 2 \times \frac{1}{2} = 3$ lattice points. This hexagonal prism has volume: $(\sqrt{3})(3/2)a^2c$.

Materials with this structure are almost always seen with 2 atoms per lattice point (see Figure 4.12): these are **hexagonal close-packed (HCP)**, and ca. 74% of the space is filled (the same as FCC). Examples are ● Zn, Mg, and Ti.

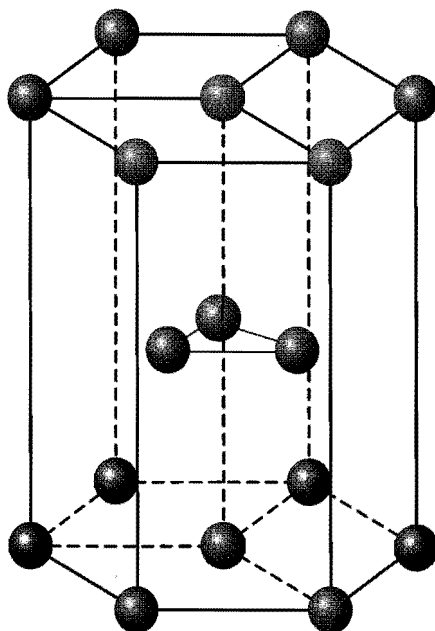
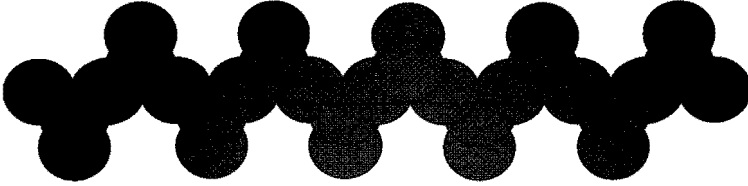


Figure 4.12. The HCP unit cell with 2 atoms per point.

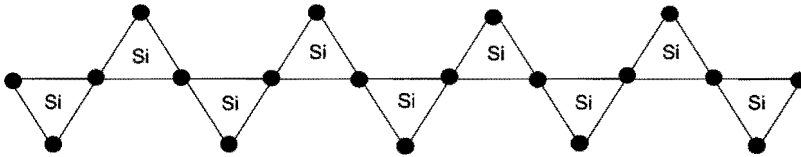
Intermezzo

A special case are the silicates: $(\text{SiO}_2)_n$. The basic unit is an SiO_4 tetrahedron, which can be connected to other silicons at all 4 corners: we then get crystalline quartz. However, when not all corners are used we can get layers (e.g. mica, clay; C in Figure below) or strands of silica (single chain, as A in Figure below, or double chain, as in B), with cations to balance the charge.

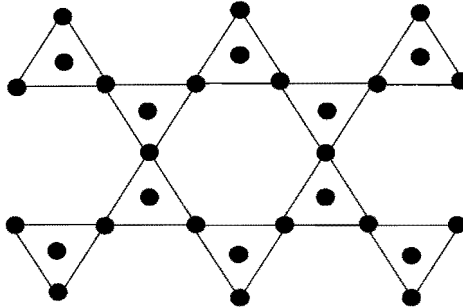
A:



B:



C:

*Intermezzo*

Classical ceramics: Clay → brick/porcelain

The common mineral feldspar (KAlSi_3O_8) can lose potassium in an acidic environment to form HAlSi_3O_8 . Basic solutions then change this to kaolinite, $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_8$, which precipitates as clay.

The structure of clay is an example of a layered silicate: there is a layer with $\text{Si}_2\text{O}_5^{2-}$ as unit, and a layer with $\text{Al}_2(\text{OH})_4^{2+}$ as unit. The interaction between the layers is weaker than the covalent bonds within the layers: clay can easily be sheared.

By heating clay to 700–900 °C it loses water, and brick or porcelain is formed:
 $2 \text{Al}_2\text{O}_3 + 4 \text{SiO}_2$.

4.4 Polymorphism and polycrystallinity

Many substances can crystallize in a number of different crystalline structures, depending on temperature, solvent, pH, etc.: they are **polymorphic**.

Example: CaCO_3 (see Figure 4.13) normally crystallizes in the most stable form, calcite (rhombohedral). This form is found in chalk and limestone. At higher temperatures, aragonite (orthorhombic) can crystallize. This form is found a lot in shells and coral. A form that is not stable, but changes into one of the others after a certain time (metastable) is vaterite (hexagonal).

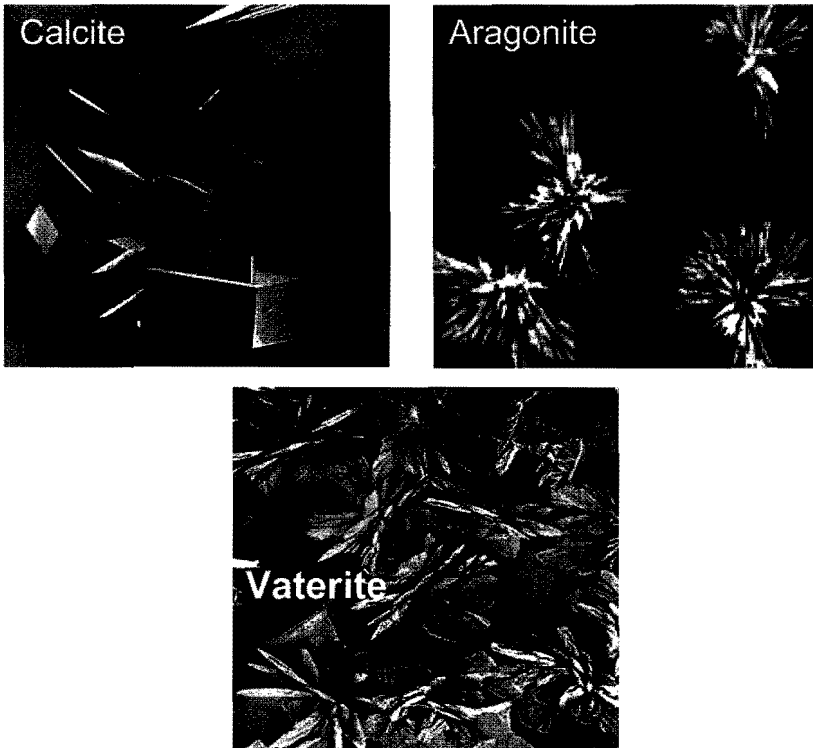


Figure 4.13. The three polymorphs of calcium carbonate.

Also important is the fact that only a few materials of reasonable size are composed of a **single crystal**: this type of compound has properties that can be predicted from the crystal structure, and will show strong differences in properties between different directions (anisotropic).

Most materials that are used in practice are **polycrystalline**: they consist of lots of small crystals (**grains**) that stick together. The effect of this is that properties are averaged out over all directions (isotropic), and that the properties of the material are also determined by the places where the crystals stick together (**grain boundaries**).

In Figure 4.14 we can see how a polycrystalline material is formed in general: crystals (squares) start growing in the melt until they meet. The resulting liquid will solidify on one of the crystals, until everything is solid in the form of grains with grain boundaries in between.

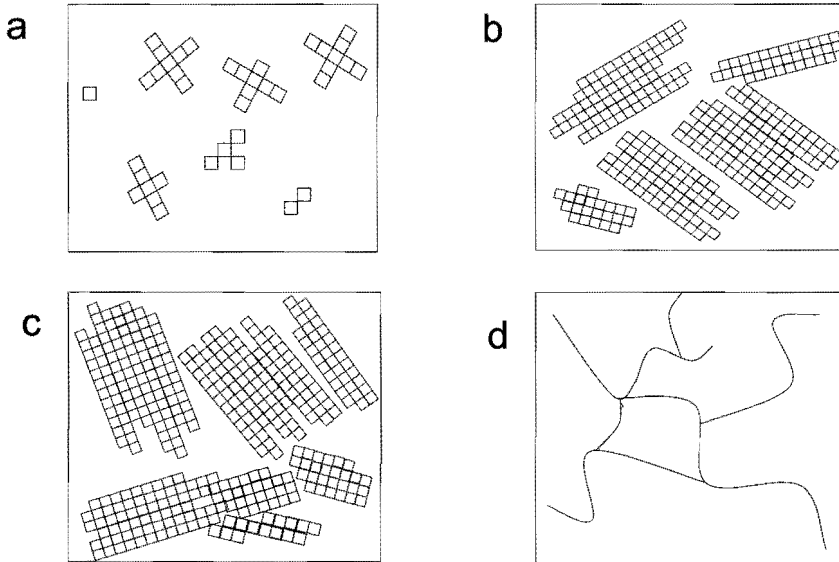


Figure 4.14. Several stages of grain formation: (a) formation of first crystals, (b, c) growth of crystals until they meet, (d) final solidification with grain boundaries.

4.5 Miller indices

In cubic crystal structures we want to be able to indicate positions, directions and planes, so we can tell in what way the structure changes upon deformation.

It is important to remember that each of these positions, directions and planes repeats in all other unit cells. Also, the origin of the coordinates can be taken at any corner of the unit cell, since they are all equivalent.

4.5.1 Positions

As can be seen in Figure 4.15, positions are indicated with x , y and z coordinates as usual, where the length of the edge of the cube is taken as the unit. The origin can be taken as any of the points of the cube, because they are all the same (the unit cell repeats in the lattice).

Example: $(0, \frac{1}{2}, -1)$ means 0 along the x -axis, $a/2$ along the y -axis, and $-a$ along the z -axis.

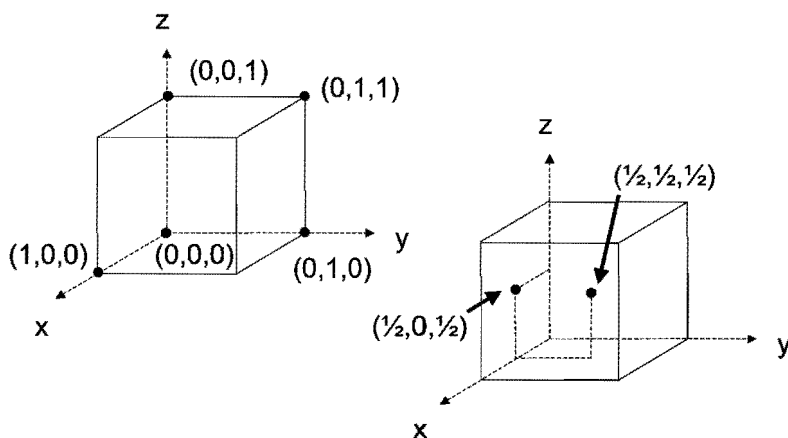


Figure 4.15. Several examples of positions in a cubic unit cell.

4.5.2 Directions

Directions are also indicated in the usual way as vectors: the difference between two points. The notation is different than normal for vectors: Only integer numbers are used, and negative numbers are indicated with a bar over the number. The integers are then written between square brackets (see Figure 4.16).

Example: the vector from $(0, 1, \frac{1}{2})$ to $(1, 0, 1)$ is normally $(1, -1, \frac{1}{2})$. Multiply by 2 to get integers: $(2, -2, 1)$. Now write this vector as: $[2\bar{2}1]$.

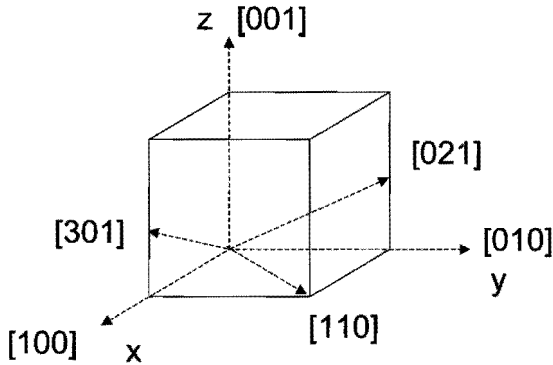
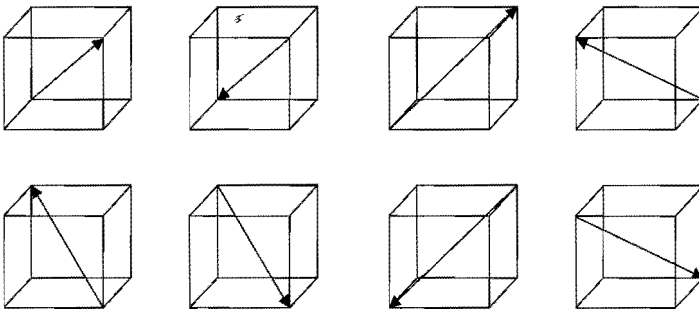


Figure 4.16. Several directions in a cubic unit cell with their Miller indices.

Since a lot of different directions in a cube are actually the same due to symmetry, they are bundled together as a family: $\langle hkl \rangle$.

Example 1: The notation $\langle 100 \rangle$ indicates all similar directions along an axis: $[100]$, $[010]$, $[001]$, $[\bar{1}00]$, $[0\bar{1}0]$, $[00\bar{1}]$.

Example 2: All body diagonals in a cube can be grouped together as $\langle 111 \rangle$.



Angles between vectors can be calculated via the so-called dot product or scalar product. When we have two vectors $\vec{A} = (a_1, a_2, a_3)$ and $\vec{B} = (b_1, b_2, b_3)$, we can calculate the dot product in two different ways:

(i) via the x-, y- and z-coordinates of both vectors: $\vec{A} \cdot \vec{B} = a_1b_1 + a_2b_2 + a_3b_3$;

(ii) via the lengths of the vectors and the angle between them:

$\vec{A} \cdot \vec{B} = |\vec{A}| |\vec{B}| \cos(\phi)$, where $|\vec{A}| = \sqrt{a_1^2 + a_2^2 + a_3^2}$ and $|\vec{B}| = \sqrt{b_1^2 + b_2^2 + b_3^2}$.

The angle ϕ between two vectors $[h_1k_1l_1]$ and $[h_2k_2l_2]$ is then given by:

$$\cos \phi = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2} \sqrt{h_2^2 + k_2^2 + l_2^2}}$$

4.5.3 Planes

For planes the notation is a bit more complex: it is easier first to show how it works for a line. Every line can be given as:

$$y = ax + b$$

However, this can also be written as:

$$ax - y = -b$$

and then as:

$$-\frac{a}{b}x + \frac{1}{b}y = 1$$

With $\mathcal{A} = -b/a$ and $\mathcal{B} = b$, we then get:

$$\frac{x}{\mathcal{A}} + \frac{y}{\mathcal{B}} = 1$$

\mathcal{A} and \mathcal{B} now represent the intercepts of the line with the axes: $x = 0$ gives $y = \mathcal{B}$ (y -axis intercept), and $y = 0$ gives $x = \mathcal{A}$ (x -axis intercept).

The same can now be done for a plane. Normally the equation for a plane is:

$$z = ax + by + c$$

but this can also be written as:

$$\frac{x}{\mathcal{A}} + \frac{y}{\mathcal{B}} + \frac{z}{\mathcal{C}} = 1$$

Again, \mathcal{A} , \mathcal{B} and \mathcal{C} are the intercepts with the x , y and z axes.

The **Miller indices** of the plane are now: $h = 1/\mathcal{A}$, $k = 1/\mathcal{B}$ and $l = 1/\mathcal{C}$, so:

$$hx + ky + lz = 1$$

The only rule is that h , k and l must be integer numbers again. The notation is then: these integers between round brackets, with negative numbers indicated by an overbar.

Note that we can not calculate \mathcal{A} , \mathcal{B} and \mathcal{C} from h , k and l : the rules given here are one-way, because the intercepts belong to one specific plane, while the Miller indices belong to an infinite family of planes (one in each unit cell). The reverse process can only be done for one specific plane (e.g. from a drawing): determine the intercepts with the axes, and calculate h , k and l from them.

In Figure 4.17, several planes are shown, together with the appropriate choice of origin (black dot) for determining the Miller indices.

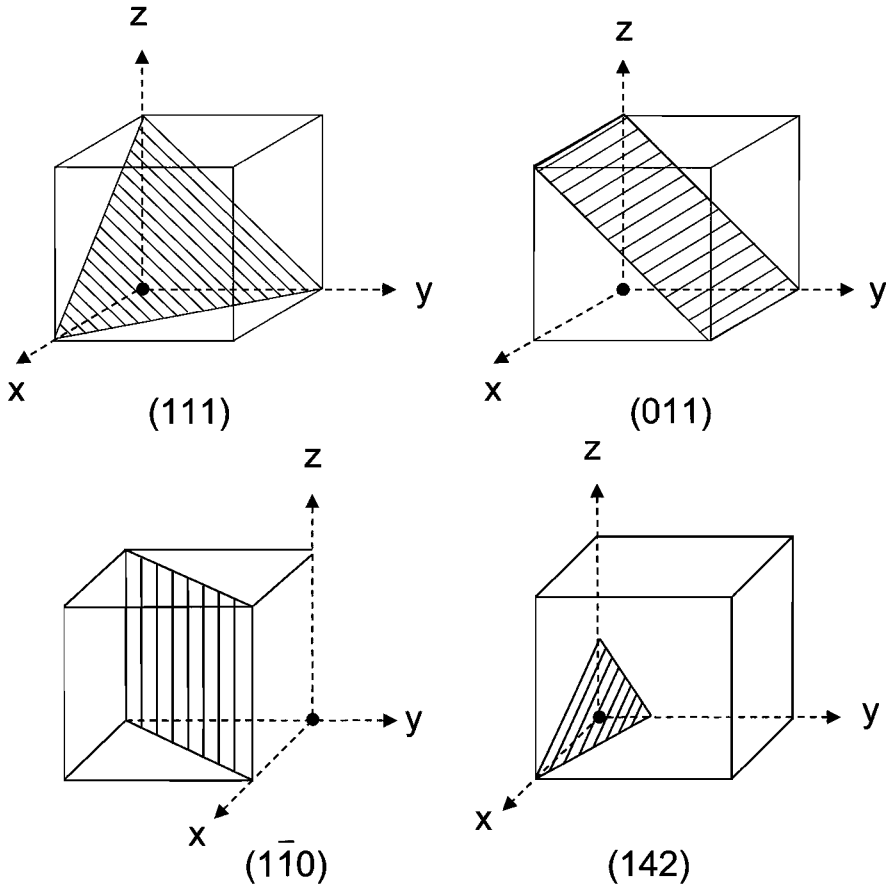
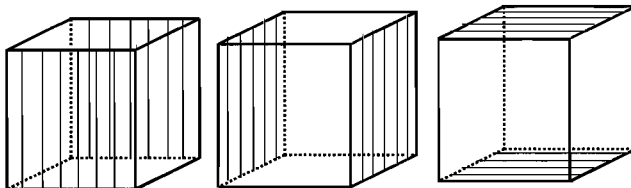


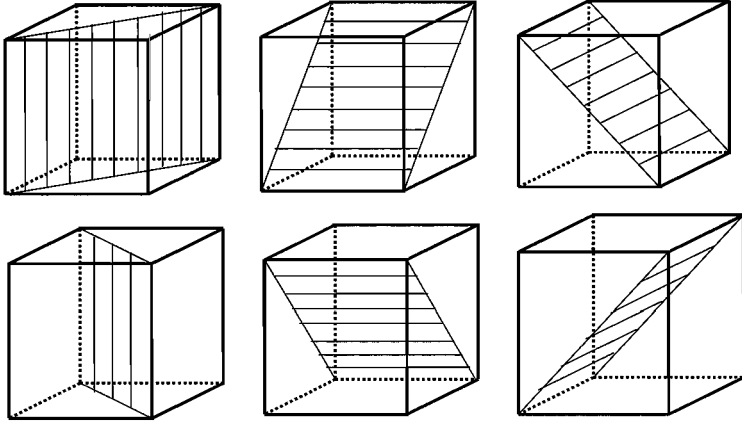
Figure 4.17. Several planes with their Miller indices. Note that the origin is not always in the same location.

Also here, a collection of symmetrically identical planes can be bundled together, in this case with the notation $\{hkl\}$.

Example 1: All side planes of the cubic unit cell can be collected as: $\{100\} = (100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1})$



Example 2: All diagonal planes together are indicated as $\{110\}$:



The advantage of this notation with Miller indices for planes is that there are two very convenient mathematical relationships now:

- The vector that is normal to a plane (hkl) is simply $[hkl]$: this vector has an angle of 90° with all the vectors in the plane (hkl) . Check this with the dot product!
- The spacing (distance) between all the planes with indices (hkl) in the various unit cells of a cubic crystal lattice with a cube edge a is given by:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

We can now also find out which planes are the most densely packed with atoms in a crystal. We will see later that these planes are important for deformations of the material: BCC– (110) ; FCC– (111) ; HCP– (0001) .

Intermezzo

For hexagonal unit cells, 4 numbers are used to indicate directions and planes. These *Miller–Bravais indices* are due to a different choice of unit vectors. *Directions*: $[uv tw]$ instead of $[u'v'w']$, with $u = n(2u' - v')$, $v = n(2v' - u')$, $t = -(u + v)$, $w = nw'$, and choose n so that the smallest integers are obtained. *Planes*: $(hkil)$ instead of (hkl) , with $i = -(h + k)$.

Intermezzo

For the study of crystal structures, we can use various techniques.

The most often used is *X-ray diffraction*: this gives the spacing d between planes of atoms, when X-rays with wavelength λ are diffracted from a crystal under an angle θ :

$$n\lambda = 2d \sin \theta$$

Individual atoms can be seen with *field ion microscopy*, *scanning tunneling microscopy* (STM), or *atomic force microscopy* (AFM).

4.6 Glasses

When the crystalline order is not present, e.g. by very rapid cooling of a melt, we get a disordered solid: a **glass**. Inorganic glasses are not very viscous liquids, as is sometimes said: they are just as solid as crystalline materials with strong bonds, but they lack order (see Figure 4.18).

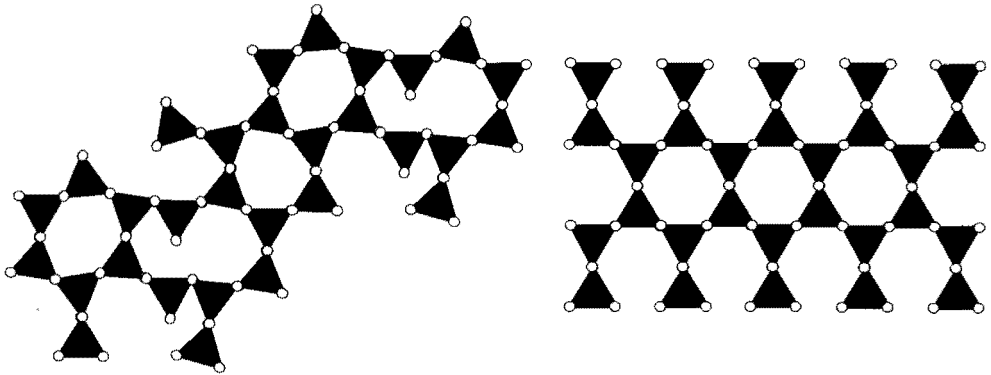


Figure 4.18. Glasses have no order in their covalent bonds (left), in contrast to a crystalline substance (right).

Glasses can be found for metals (metallic glasses), but mostly we see this for ceramic oxides. They can be completely glassy, or a mixture: the glass–ceramics.

Some polymers at low temperatures are actually also glasses, but their behaviour is so different that we will treat them separately.

Most oxide glasses are based on silicon oxide (SiO_2 , sand), but various other oxides can be mixed in to change the properties of the glass. Examples are: Al_2O_3 (fibreglass), B_2O_3 (electrical applications), Na_2O (lamp bulbs), CaO (fibreglass), and PbO (lamp tubing, crystal glass).

4.6.1 Glass temperature

The difference between the glassy and crystalline states of a material can be seen most easily when the volume is followed as a function of temperature during cooling (see Figure 4.19).

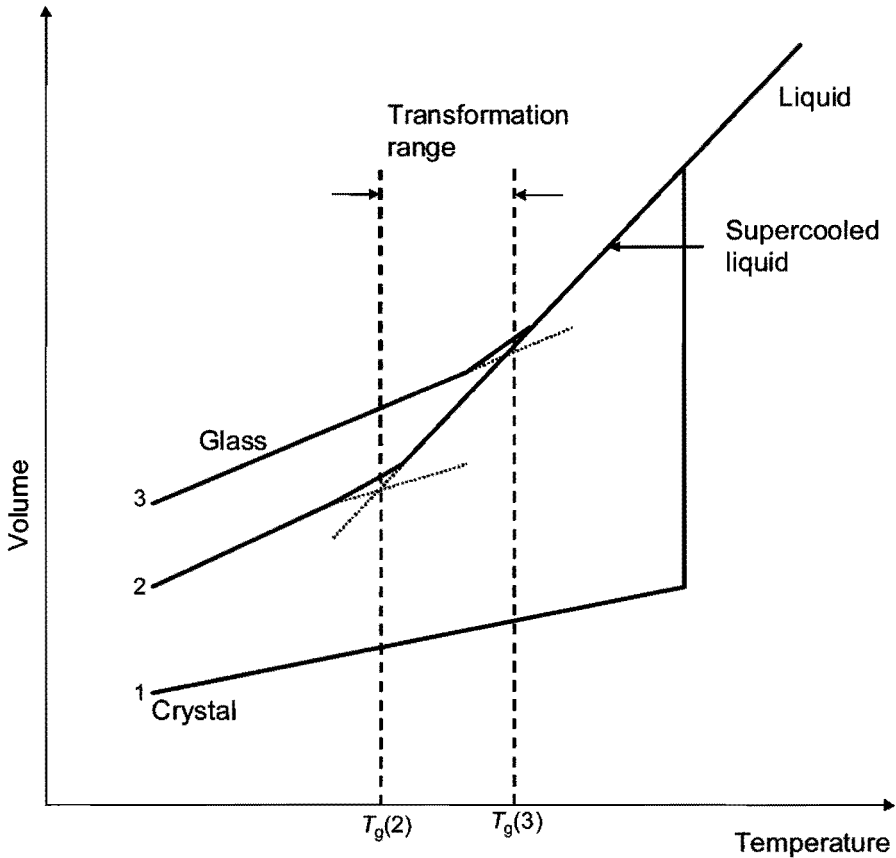
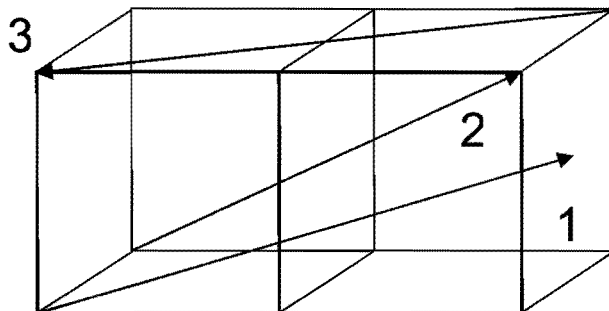


Figure 4.19. Whereas crystalline substances (1) show a clear melting point, glasses (2,3) show a transition at a variable temperature (2: slow cooling, 3: rapid cooling).

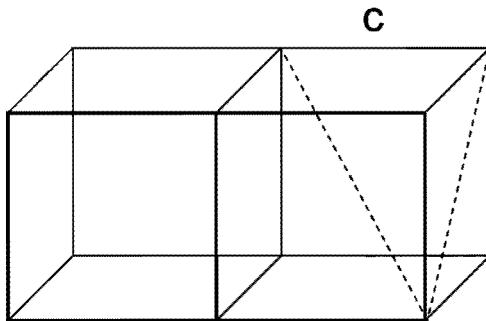
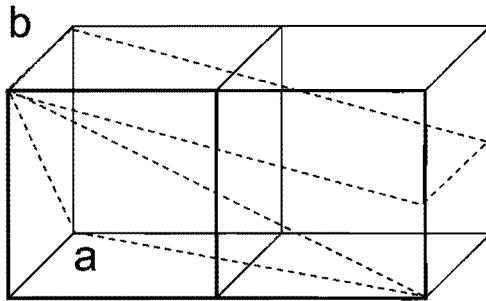
A crystalline material solidifies at one specific temperature (**melting temperature**, T_m), with a clear decrease in volume. For glasses, the liquid melt is first supercooled, and then shows a transition to the glassy state at the **glass temperature** (T_g). This glass temperature is dependent on the cooling rate: faster cooling (3 in Figure 4.19) gives a higher T_g . The volume does decrease during supercooling and glass formation, but glasses always have a larger volume than crystalline solids, because the packing of atoms is not so efficient.

Problems

- 4.1.a. Caesium metal has a BCC structure with a lattice parameter of 0.6080 nm. Calculate the atomic radius.
- b. Thorium metal has an FCC structure with a lattice parameter of 0.5085 nm. Calculate the atomic radius.
- 4.2.a. Rhodium has a lattice parameter of 0.3805 nm and the atomic radius is 0.134 nm. Calculate from this whether this metal has a BCC or an FCC structure.
- b. Niobium has a lattice parameter of 0.3307 nm and the atomic radius is 0.147 nm. Calculate from this whether this metal has a BCC or an FCC structure.
- 4.3. If the atomic radius of Al is 0.143 nm, calculate the volume of its unit cell in cubic meters.
- 4.4. Calculate the number of atoms per cubic meter in Al.
- 4.5. Titanium undergoes a change from HCP to BCC upon heating above 882 °C. Assume that in HCP Ti, $a = 0.295$ nm and $c = 0.468$ nm, while in BCC Ti, $a = 0.332$ nm and 1 atom/point. What is the fractional volume change when HCP Ti transforms to BCC Ti?
- 4.6. Calculate the percentage volume change when FCC (γ) iron ($a = 0.365$ nm) transforms to BCC (δ) iron ($a = 0.293$ nm) at 1394 °C.
- 4.7. Calculate the theoretical density of beryllium from the fact that it is HCP with $a = 0.2286$ nm and $c = 0.3584$ nm.
- 4.8. CaO has a rock salt structure with a lattice parameter of 0.480 nm. Determine the theoretical density of CaO and the number of atoms per unit cell.
- 4.9. CdS has a cubic unit cell, and from X-ray diffraction data it is known that the cell edge length is 0.582 nm.
- a. If the measured density is 4.82 g/cm^3 , how many Cd^{2+} and S^{2-} ions are there per unit cell?
- b. Based on your answer in a., what type of cubic structure is present in CdS?
- 4.10. What are the Miller indices of the directions 1, 2, and 3 in the Figure below?



4.11. What are the Miller indices of the planes *a*, *b*, and *c* in the Figures below?



4.12. Select all of the directions that lie in the (111) plane of a cubic crystal:

- a. $[111]$ b. $[\bar{1}11]$ c. $[100]$ d. $[110]$ e. $[\bar{1}12]$
 f. $[\bar{1}01]$ g. $[3\bar{2}1]$ h. $[\bar{2}11]$ i. $[5\bar{2}\bar{3}]$ j. $[102]$

4.13.a. Determine the Miller indices of the plane that passes through the three points $(0,0,1)$, $(\frac{1}{2},1,\frac{1}{2})$, and $(1,\frac{1}{2},\frac{1}{2})$ within a cubic lattice.

- b. What are the coordinates of the intercept points on the *x*, *y* and *z* axes?
 c. What are the Miller indices of the direction connecting the last two points in problem a.?

4.14.* Calculate the density of a silicon single crystal with a diamond-cubic structure. Does it fit with the experimental value?

4.15.* We are studying a single crystal of chromium (Cr).

- a. Calculate the radius of Cr from the lattice parameter. Does this fit with the kind of bond?
 b. Calculate the number of atoms in the unit cell from the density, and check with the expected value.

4.16.* Give a vector in the plane (142), and explain how you obtain it.

5 Inorganic Materials II: Mechanical properties and structural defects

Now that we know the structures that are expected for inorganic materials, we can see what the relation is with their mechanical properties.

We have already looked at the Young's modulus (stiffness) in Chapter 3, so here we will study yield and fracture.

Learning without thought is lost; thought without learning is dangerous.

孔夫子 or Kǒng Fū-Zǐ or Kǒng Zǐ (Master Kǒng), "Confucius"
(551–479 BCE)

5.1 Yield and defects

5.1.1 Yield and shearing

Yield occurs when the material is deformed permanently, so we must move atoms by breaking bonds and reforming them in another location. In a crystal, this can happen most easily when we move different planes of atoms parallel to each other (shearing). This usually happens along the planes with the highest density of atoms, since then the bonds can reform between the planes after only a small movement during the shearing process.

It is now important to realize that during a tensile test, where we stretch the material with a force perpendicular to the cross section of the test bar, shearing forces still occur. These are the forces that result in yield.

We can see this first in a very simplified, two-dimensional case. This is *not* a realistic model: do *not* use this for problems or examinations!

The external force F leads to a tensile stress: $\sigma = F/A$. Inside the material, shearing can occur when we look at a cross section with an angle θ to the normal cross section, which is perpendicular to F . The area of this tilted cross section is:

$$A' = \frac{A}{\cos \theta}$$

The force component parallel to this cross section is given by:

$$F' = F \sin \theta$$

Therefore we can write for the shearing force parallel to A' :

$$\tau = \frac{F'}{A'} = \sigma \cos \theta \sin \theta = \frac{1}{2} \sigma \sin 2\theta$$

This shearing force is then maximal for $\theta = 45^\circ$:

$$\tau_{\max} = \sigma/2$$

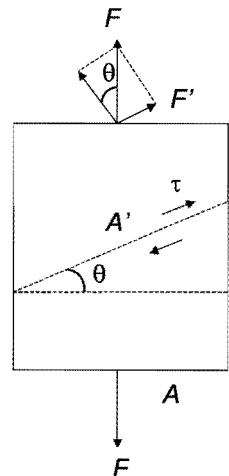
This value is often referred to as the tensile yield stress:

$$\sigma_Y = 2\tau_{\max}$$

Also, one can speak about the shear yield strength:

$$\tau = \sigma_Y/2$$

However, real materials are three-dimensional, which means that the analysis above is incomplete. What exactly happens at the microlevel is different for materials that consist of a single crystal, and materials that are polycrystalline. We will look at the single crystals first.



5.1.2 Single crystals

In a single crystal during stress, yield can occur by shearing along planes in the crystal structure that are closest to the 45° angle. This indeed happens for single-crystal materials, as can be seen in Figure 5.1.

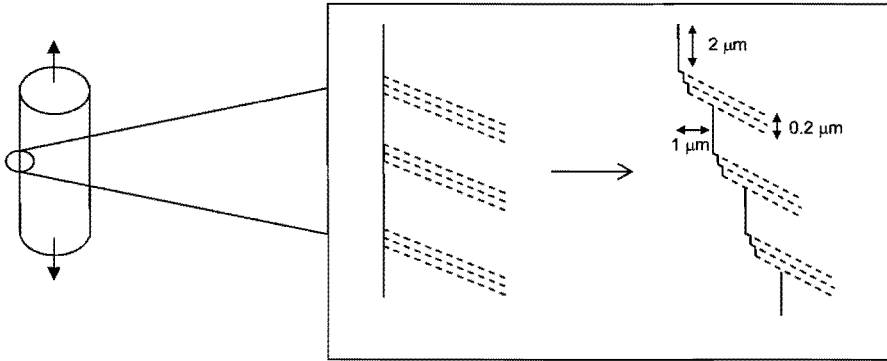


Figure 5.1. Stretching a single-crystal material leads to sliding of layers of the material in roughly 45° angles.

For a specific crystal structure, we can define a **slip system**: a combination of a *plane* along which shear will occur, and a *direction* in that plane in which shear will occur (see Figure 5.2). The slip planes will be the most densely packed plane in the crystal lattice, and the slip direction will be the most densely packed direction. In that way, the smallest steps have to be made before movement occurs.

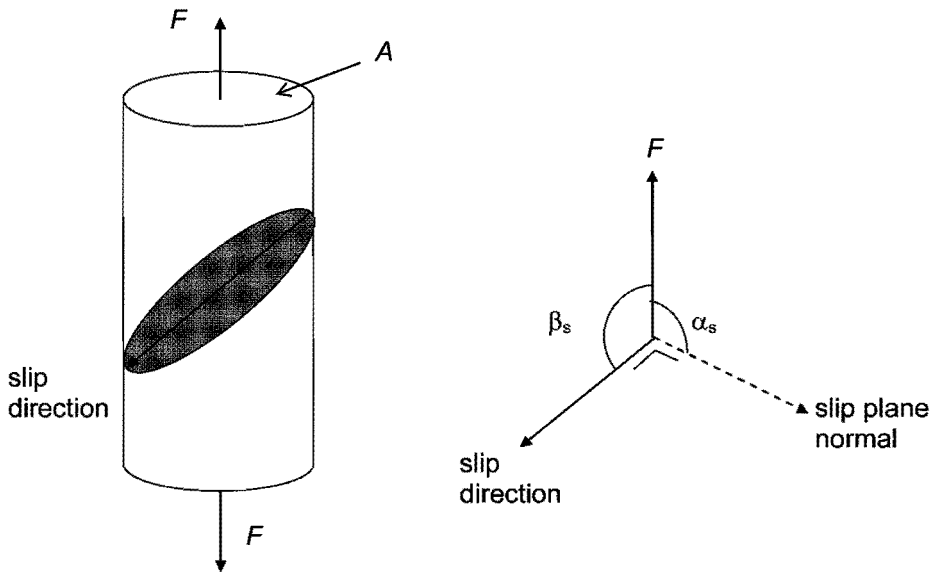


Figure 5.2. The slip system in a single crystalline material.

We now have two different angles: α_s between the applied force and the slip plane (or rather, the normal vector of the plane), and β_s between the force and the slip direction. α_s is the same as θ in the two-dimensional case, so we have the same formula for A' , but β_s is new (it is the component of the force along the slip direction). The angles are in different planes, so they can independently assume any value. From the Miller indices of the slip plane normal, the slip direction, and the applied force we can calculate the cosines of α_s and β_s with the dot product (see section 4.5).

The internal shear stress in the slip system (τ) can then be written as a function of the externally applied stress ($\sigma = F/A$):

$$\tau = \frac{F'}{A'} = \frac{F \cos \beta_s}{A / \cos \alpha_s} = \sigma \cos \alpha_s \cos \beta_s$$

For a specific single-crystal material, a **critical shear stress** (τ_C) can be measured. This is the stress where yield first occurs in a slip system:

$$\sigma_Y = \frac{\tau_C}{\cos \alpha_s \cos \beta_s}$$

Example: Silver has an FCC structure, where the slip system is $\{111\} \langle 1\bar{1}0 \rangle$, with a critical stress $\tau_C = 0.58$ MPa.

See Table 3 in Appendix E for an overview of slip systems and critical stresses. In general, FCC structures have more slip systems than BCC or HCP, and therefore materials with an FCC crystal structure will be more ductile.

What can we now predict theoretically for these critical shearing forces? What must happen during yield is the sliding of layers of atoms over each other (see Figure 5.3). The first step is the (elastic) stretching of the bonds between the atoms to "lift up" the top layer, so it can move. This is the difficult step, so it will determine the critical stress.

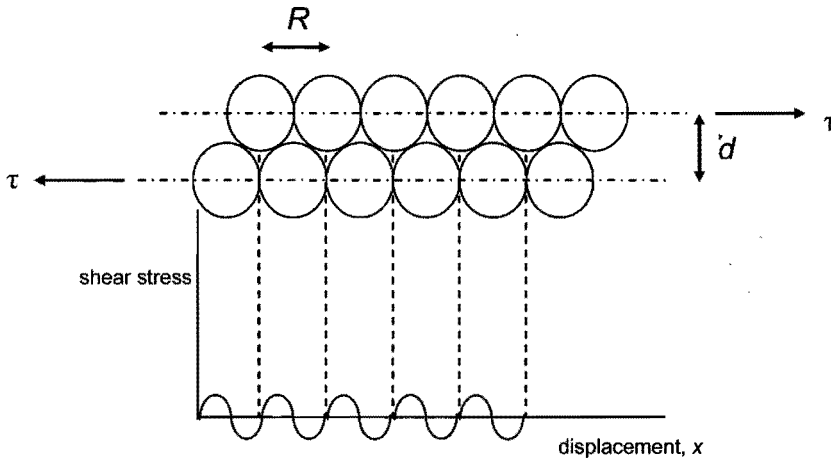


Figure 5.3. A simple model for plastic deformation in a perfect crystal.

For atoms with an interatomic distance R and layers with spacing d , a small displacement x will lead to a shearing stress:

$$\tau = G\gamma = \frac{Gx}{d} \quad (\text{with: } \gamma \approx \tan(\gamma) = x/d)$$

As a simple model we can now write for the shear stress during the movement:

$$\tau = \tau_{\max} \sin \frac{2\pi x}{R}$$

For small values of x we can write:

$$\tau \approx \frac{\tau_{\max} 2\pi x}{R}$$

Then we can calculate for the theoretically expected shear yield strength:

$$\tau_{\max} = \frac{GR}{2\pi d}$$

We now have a prediction that the yield strength is related to an elastic property: the shear modulus. (This is why in section 2.4 we gave yield strength as σ_Y/E .)

Example: In an FCC crystal with edge a , and 1 atom per point, we find that the atoms have a distance $R = a/\sqrt{2}$. For a (111)-plane in this crystal we can calculate the spacing $d = a/\sqrt{3}$, so we then predict: $\tau_{\max} \approx 0.2G$.

When we look e.g. at silver ($G = 19.7$ GPa), we would now predict: $\tau_{\max} = 4$ GPa, so the yield stress would then be $\sigma_Y = 8$ GPa.

A more sophisticated model for the forces between the atoms predicts a somewhat lower value for the shear yield strength of silver: $\tau_{\max} = 0.77$ GPa.

But the experimental value for the critical shear stress of silver along the (111)-plane is 3 orders of magnitude lower: 0.00058 GPa. This is very typical, as can be seen from these examples (first predicted and then measured values):

Al	900 vs. 1 MPa
Cu	1200 vs. 0.7 MPa
Zn	1300 vs. 0.2 MPa
α -Fe	6900 vs. 28 MPa

This shows that there must be **defects** in the ideal crystal structure that determine the mechanical properties much more than the ideal crystal structure.

5.1.3 Defects

There are lots of **point defects** (zero-dimensional) that can occur in a crystal structure. In Figure 5.4 we see several of them:

- vacancies: missing atoms in the lattice
- interstitials: additional atoms inserted in the lattice
- impurities: atoms that are replaced by others
- ionic defects: Schottky and Frenkel defects, where the overall charge must remain neutral.

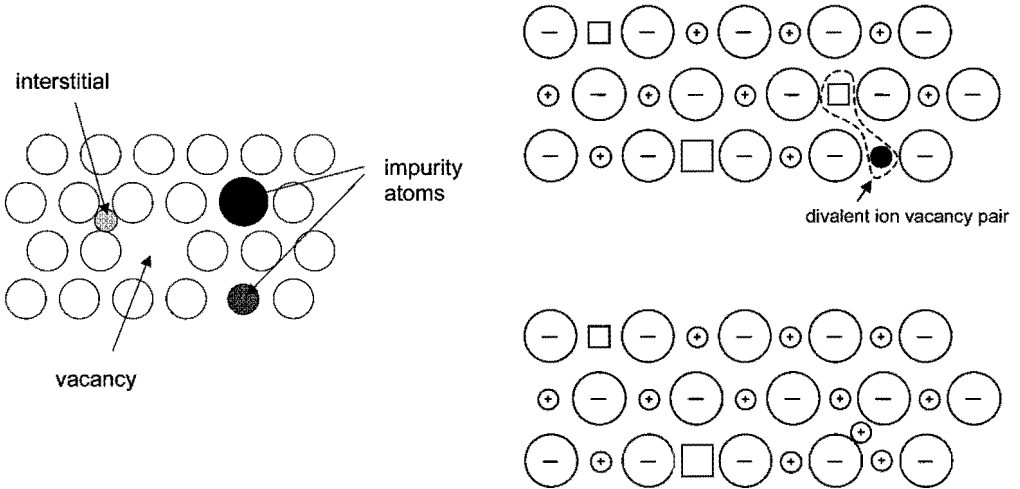


Figure 5.4. Point defects in a crystal lattice: vacancies, interstitials and replacements (left); Schottky and Frenkel defects (top right and bottom right respectively).

More important for the mechanical properties are the **line defects** (one-dimensional), or **dislocations**. There are two types of dislocation: **edge** and **screw**, as can be seen in Figure 5.5.

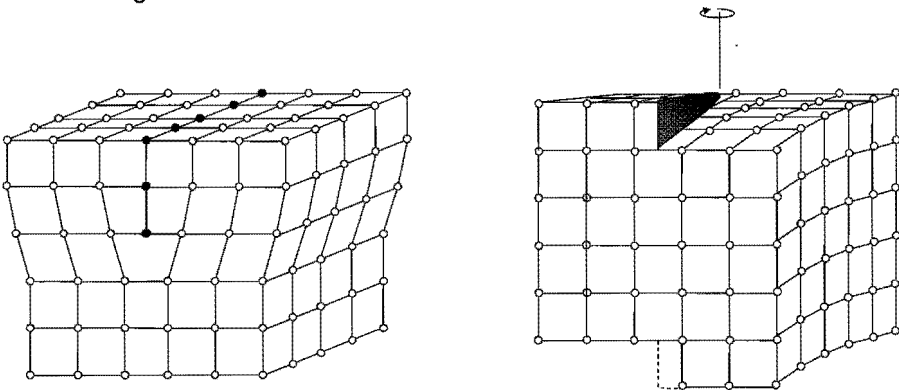


Figure 5.5. One-dimensional defects can be present as linear edge dislocations, or helical screw dislocations.

In addition, in polycrystalline materials there are the places where the crystals (grains) stick together: the grain boundaries. These are **planar** (two-dimensional) **defects**. The structure of the grain boundaries is often called the **microstructure** or **morphology** of the material, which is strongly dependent on the processing.

Finally, when all crystalline order is gone, we have a three-dimensional defect: a glass.

So, a material can have different types of defects:

- zero-dimensional = point defects
- one-dimensional = line defects (dislocations)
- two-dimensional = plane defects (grain boundaries)
- three-dimensional = volume defects (glasses).

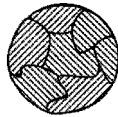
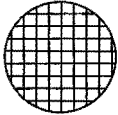

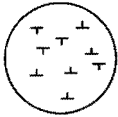
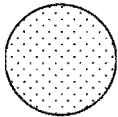
Intermezzo

How can one see defects?

The presence of dislocations, and the microstructure or morphology can be studied with various techniques: optical microscopy, SEM, TEM, and AFM.

TEM can show lines of dislocations, electron microscopy and optical microscopy can show grain boundaries.

Of course, one always has to look at various length scales when considering the effects of defects on the mechanical properties of a material.

Typical length scale	Structural feature	
0.1 mm	Grain structure	
10 μm	Single grain	
0.2 μm	Dislocation cells	
10 nm	Individual dislocations	
5 Å	Atoms / crystal structure	

5.1.4 Mobility of dislocations

Dislocations are especially important for the mechanical properties of crystalline materials, since they can easily move through the crystal lattice, thereby causing yield. For the movement of a dislocation, fewer bonds have to be broken and remade at the same time, compared to movement of planes of atoms (see Figure 5.6).

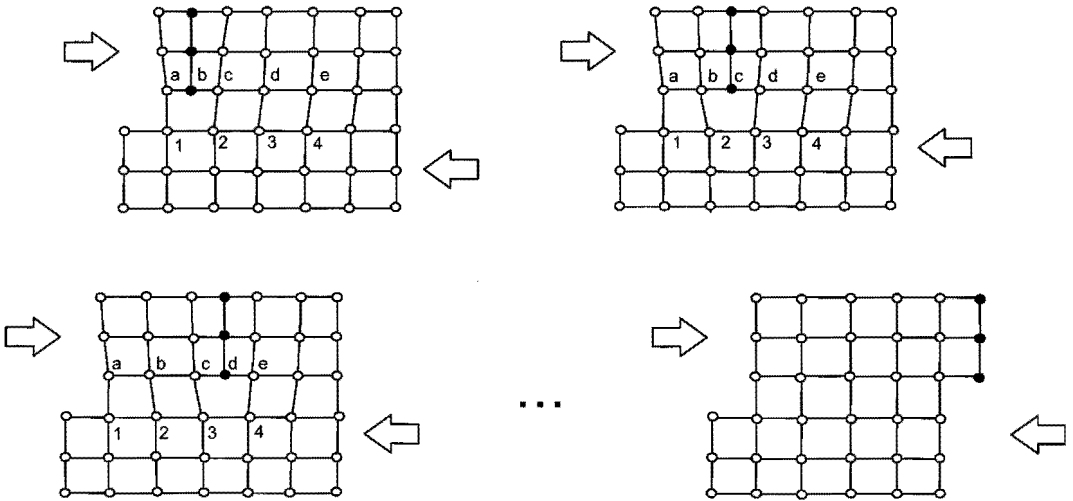


Figure 5.6. Movement of dislocations due to shear stress leads to plastic deformation.

The difference between the yield of crystalline ceramics (brittle) and crystalline metals (ductile) can be explained mostly by the difference in mobility of dislocations. When a dislocation moves, bonds must be broken and reformed with different atoms. For metals, this is very easy, because the metallic bond is the same for all directions (electron sea). In ceramics, the ionic or covalent bonds are dependent on the direction, so it is more difficult to switch from one atom to the next.

In *metals*, the dislocations are therefore very mobile, so plastic deformation (yield) is very easy: metals yield before they break, both in tension and in compression. The typical stress necessary to move dislocations in metals is $10^{-4}E$ to $10^{-3}E$. Since ductile fracture in metals also involves plastic deformation, the tensile stress of metals (σ_T) is also determined by the mobility of the dislocations: when σ_Y goes up or down, so does σ_T .

In *ceramics* the dislocations are much less mobile, and yield is more difficult. Ceramics normally break before they yield, although in compression yield is possible, since the material cannot break so easily then. (During bending, there are both tension and compression, and ceramics will then fail on the stretched side.) The typical stress necessary for moving dislocations is $10^{-3}E$ for ionic bonds, and $10^{-3}E$ to $10^{-2}E$ for covalent bonds. The covalent network ceramics are therefore the most brittle (highest σ_Y). Fracture is usually brittle (see section 5.2).

So, we see the following very important relationship between micro-, meso- and macroscale:

Directionality of bonds \rightarrow Mobility of dislocations \rightarrow Yield stress
Tensile stress (metals)

5.1.5 Microscopic anisotropy vs. macroscopic isotropy

We now come back again to the difference between single crystals and polycrystalline materials. Single crystals are usually anisotropic: they have different mechanical properties in different directions. In polycrystalline materials, we see an averaged property: the material is isotropic.

Example: BCC α -Fe has different Young's moduli in different directions: $E_{[001]} = 125$ GPa, $E_{[111]} = 273$ GPa, and $E_{[110]} = 210$ GPa.

Polycrystalline α -Fe has a modulus $E = 210$ GPa in all directions.

Also for the yield stress, we see that the grain boundaries are the weak spots of a polycrystalline substance: instead of the critical shear stress in a slip system, we have to look at the shear stress where the grain boundaries start sliding: τ_{gb} .

Although there are a lot of grain boundaries in a polycrystalline material with all kinds of orientations, the shear will be strongest along the 45° angle, so these grain boundaries will move first. However, the movement of dislocations usually dominates the yield process.

5.2 Brittle fracture and crack growth

When a material breaks, atomic bonds are broken, and new surfaces are created. It should therefore be possible to understand tensile strength in terms of interactions between atoms. Since the behaviour of surfaces is also very important for biocompatibility, we shall treat it in some more detail first.

5.2.1 Surface tension

The atoms on surfaces have a higher energy than the atoms in the bulk, since they lack bonds with other atoms that atoms in the bulk have (see Figure 5.7).

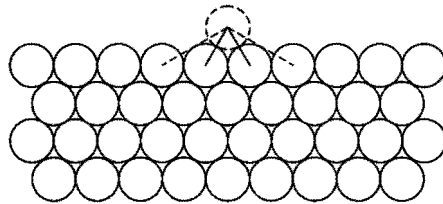


Figure 5.7. Atoms at the surface miss bonds compared to bulk atoms.

Therefore there is always an excess surface energy (on the order of $1\text{--}10\text{ J/m}^2$). A material will therefore always try to minimize its surface area if possible.

Of course, the surface energy depends also on the medium (air, water) with which the surface makes contact: when the atoms on the surface have a good interaction (bonds) with the molecules in the medium, the surface energy will be lower. In most tables, the surface energy is given with air as the medium (almost no interaction possible), but in general the surface energy should refer to an interface between two materials.

The excess surface energy is called the **surface tension** γ . The unit for γ can be as for energy [J/m^2], or as for force [N/m] (these units are identical).

The interaction with liquids (water, blood) is very important for biomedical materials, so we will introduce some properties related to this. We will see in section 6.1 that we can use these properties also in more general situations. When a drop of liquid (L) sits on a solid surface (S) in the presence of air (G), the **contact angle** θ is determined by the surface tensions γ_{SG} , γ_{LG} , and γ_{SL} (see Figure 5.8).

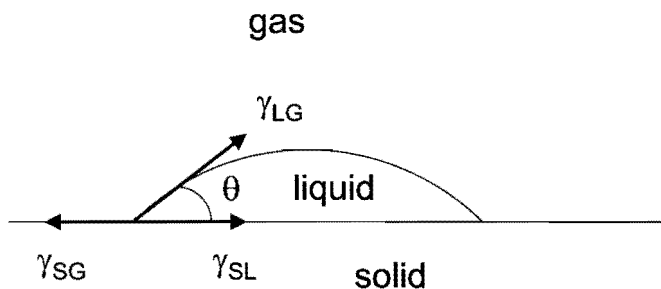


Figure 5.8. A drop of liquid on a surface has a contact angle that is determined by the surface tensions.

This experiment can therefore be used to determine one of the surface tensions, when the two others are known:

$$\gamma_{SG} = \gamma_{LS} + \gamma_{LG} \cos \theta$$

One speaks about **wetting** of the surface (film formation) when $\theta = 0^\circ$, and **dewetting** (formation of drops) when $\theta = 180^\circ$.

For wetting one should have:

$$\gamma_{SG} = \gamma_{LS} + \gamma_{LG}$$

For dewetting one should have:

$$\gamma_{SG} = \gamma_{LS} - \gamma_{LG}$$

The **cohesion** of a material A is the work necessary to create two new surfaces (usually relative to air, but this may be different in a biomedical case):

$$W_{c,A} = 2\gamma_A$$

The **adhesion** between two materials A and B is the work necessary to break open a common interface:

$$W_{a,AB} = \gamma_A + \gamma_B - \gamma_{AB}$$

To see whether a material B will form a film on a surface of material A, it is useful to calculate the **spreading coefficient** of B on A:

$$S_{BA} = W_{a,AB} - W_{c,B} = \gamma_A - \gamma_B - \gamma_{AB}$$

If $S_{BA} > 0$, a film of B will be formed on the surface of A, while for $S_{BA} < 0$ drops of B will be formed on A.

Example: Water has $\gamma = 72.75 \text{ mJ/m}^2$, and n-octane has $\gamma = 21.8 \text{ mJ/m}^2$ (both relative to air). The interface energy between water and n-octane is 50.8 mJ/m^2 . For n-octane on water we now find: $S_{ow} = 0.15 \text{ mJ/m}^2 > 0$, so n-octane will form a film on water.

When a mixture of materials is used (e.g. alloys of metals), we must realize that the component with the lowest γ will be more concentrated on the surface, since then the total surface energy of the material will be lower. Therefore, the **bulk composition** is not always the same as the **surface composition**. This is very important for biomedical applications. Of course, the surface atoms can also react more easily with the environment: titanium is e.g. always covered with a layer of TiO_2 due to reaction with air. This layer will behave quite differently than bulk Ti.

5.2.2 Orowan model

There is a simple model (the Orowan model) to estimate the tensile stress of a material from its surface energy. As we saw before, brittle fracture involves the creation of two new surfaces, so it costs energy:

$$E_{\text{fract}} = 2\gamma A$$

We would like to express this in terms of stress and strain. We assume a perfectly crystalline material, and want to separate two layers of atoms, which are perpendicular to the stress. Normally the atoms are situated at a distance R_0 , and this has to be stretched by an additional distance R_1 before the bond can be broken (see Figure 5.9). The necessary stress is approximated with a sine function.

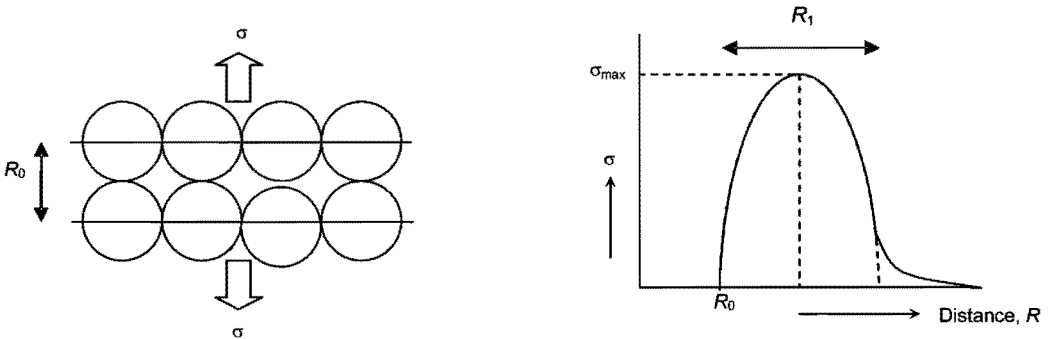


Figure 5.9. Separating two layers of atoms will lead to an increasing stress.

As can be seen in Appendix M, the Orowan model yields a maximum stress (which is also the tensile stress) given by:

$$\sigma_T = \sigma_{\text{max}} = \sqrt{\frac{E\gamma}{R_0}}$$

Experimentally we often find that $R_1 \approx R_0$, so $\gamma \approx ER_0/\pi^2$ (see Appendix M), and we then have a tensile stress:

$$\sigma_T \approx \frac{E}{\pi} \approx \frac{E}{3}$$

This is the reason that tensile strength is often given as the ratio σ_T/E : from this theory we expect this to be the same value for all crystalline materials.

We can use better models for the forces between atoms, which lead to somewhat lower values for the tensile stress: $E/8$ to $E/15$.

However, all these predictions are far too high: for iron we have $E = 211$ GPa, which predicts that $\sigma_T = 14\text{--}67$ GPa, while we find experimentally that $\sigma_T = 0.1$ GPa for bulk iron. For iron **whiskers** (small needle-shaped single crystals) we find a much higher tensile strength (13 GPa), but it is still lower than predicted. Obviously, something is wrong. In general, a higher tensile strength is found for fibres and whiskers, as shown in Figure 5.10.

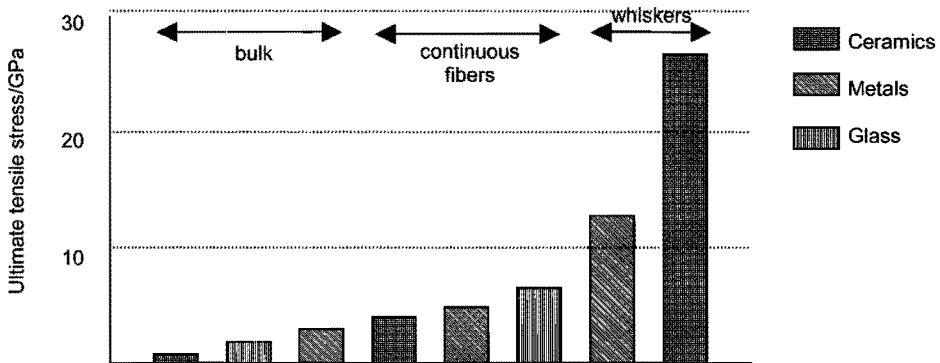


Figure 5.10. The tensile strength of materials depends on their dimensions.

The same was found by Griffith and others (e.g. Gordon) for fracture in glass fibres: the tensile strength is larger when the diameter is smaller (especially under $10\ \mu\text{m}$). It was observed that the fracture was caused by small **cracks** on the surface of the glass, which needed a minimum size to start growing. Because during the growth of the cracks only a few bonds were broken at the same time, a low stress was enough for complete fracture. Below a certain diameter of the glass fibre, the cracks were too small to start growing, and fracture only happened when the bonds between the atoms broke all at the same time, just as in the Orwan model. By extrapolation to very low diameter (see Figure 5.11), Griffith indeed found a tensile strength of 11 GPa, which nicely agrees with the theoretical value of 14 GPa for the material he used. For quite thick fibres, he found the same strength as for bulk glass: 170 MPa.

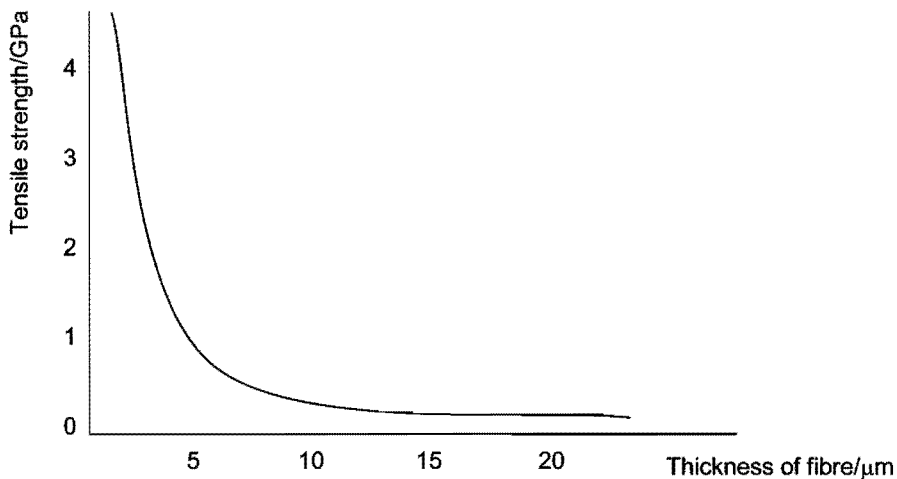


Figure 5.11. The tensile strength of glass fibres is inversely proportional to the diameter.

For whiskers of Si and ZnO a similar relation between tensile strength and diameter was found. Since whiskers are perfect single crystals, we do not have surface cracks here, but fracture starts at the “steps” on the surface where new layers of atoms start. When the surface of a material was made so smooth that steps do not occur, the tensile strength went up in value. For normal, polycrystalline materials the cracks can start on the grain boundaries, which are weak spots.

So, the tensile strength of a material is completely determined by the possibility of small cracks or imperfections to start growing.

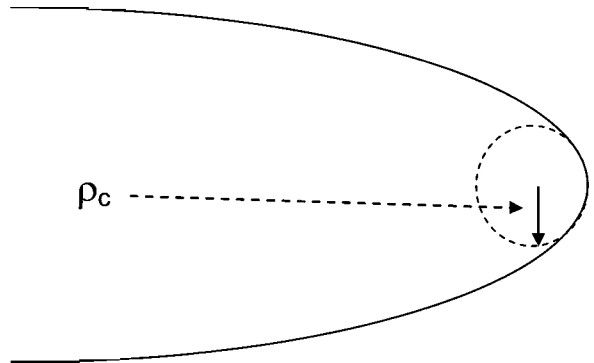
5.2.3 Stress concentrations

When analyzing the growth of crack in a material, it was found by Inglis that there must be **stress concentrations** at the end of the cracks, partly because the stress through the material is carried by a smaller surface. This increased stress leads to an unexpectedly quick plastic deformation (yield) in metals, or easier fracture in ceramics.

In Figure 5.12, c is the depth of a crack on the surface, or it is *half* of the length of an interior crack. ρ_c is the radius of a circle that fits in the tip of the crack (the radius of curvature): a sharp crack has a small ρ_c , and a blunt crack has a large ρ_c . The stress applied that is from the outside is $\sigma_a = F/A_0$, but the real stress at the tip of the crack (σ_{int}) is much higher:

$$\sigma_{int} = 2\sigma_a \sqrt{\frac{c}{\rho_c}}$$

When the crack is exactly circular (as seen from the side), then $\rho_c = c$, and $\sigma_{int} = 2\sigma_a$. For most cracks, however, the shape is elliptical with a sharp tip, and $\rho_c \ll c$, so $\sigma_{int} \gg \sigma_a$.



These stress concentrations can lead to crack blunting in metals: plastic deformation changes the shape of the crack tip, thus lowering the internal stress. However, in ceramics the stress concentrations are expected to cause growth of the cracks, and materials would break very easily. This is obviously not always true, and Griffith proposed a model to show why this is not the case.

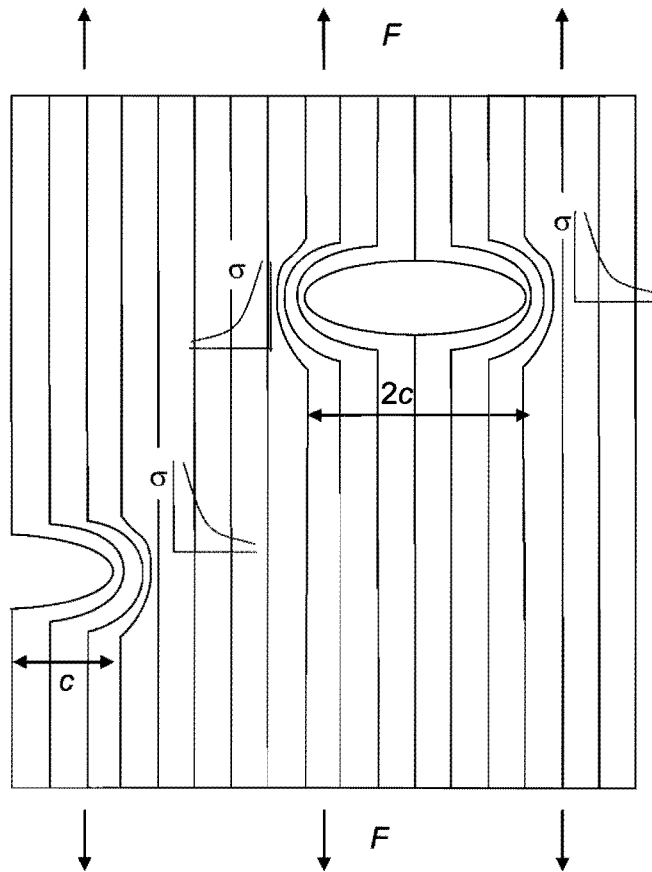


Figure 5.12. External or internal cracks in a material lead to much higher internal stresses at the crack tips.

5.2.4 Griffith model for brittle fracture

Griffith realized that the energy associated with a crack is determined by two terms: (i) the energy increases because two new surfaces are created, and the longer the crack, the more surface there is; (ii) in an area around the crack—except the tips of course—the material is no longer stressed, and elastic energy is released.

In a plate of unit thickness (see Figure 5.13), the new surface are created by an internal crack of length $2c$ is $4c$ (both sides of the crack), and the area that relaxes around the crack was found to be ca. $2\pi c^2$. This then leads to the following expression for the total energy of the crack:

$$E_{\text{crack}} = 4c\gamma - \frac{\pi c^2 \sigma^2}{E} \quad [\text{J/m}]$$

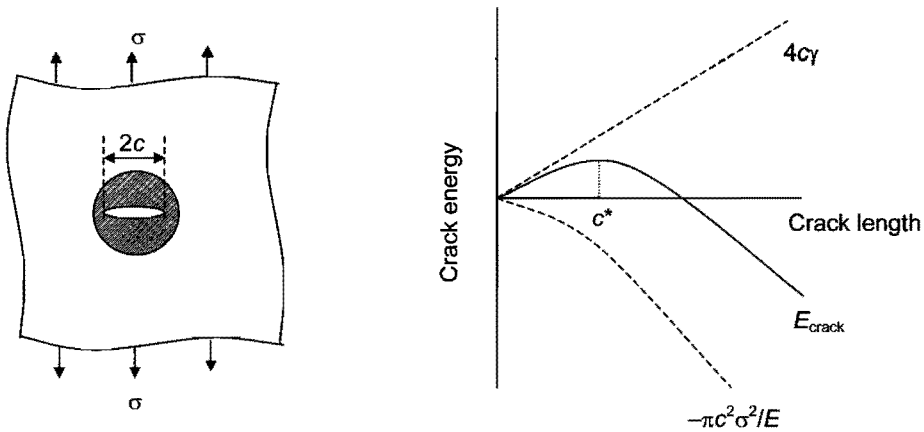


Figure 5.13. A growing crack first increases in energy, but then decreases again due to stress relaxation in the shaded area around the crack.

This means that the growing crack first increases in energy, and only starts growing spontaneously (decreasing energy), when a certain **critical crack length** is passed.

The critical crack length is reached for the maximum energy ($dE_{\text{crack}}/dc = 0$). This gives for the critical length of the cracks at a certain applied stress σ :

$$c^* = \frac{2\gamma E}{\pi\sigma^2} \text{ [m]}$$

When cracks are larger than c^* , the stress σ will lead to fracture.

Another way to look at this formula is to calculate the minimum applied stress needed to make a crack of length c start to grow: the **critical stress**.

$$\sigma^* = \sqrt{\frac{2E\gamma}{\pi c}} \text{ [Pa]}$$

Now, when the applied stress is larger than σ^* , the cracks will start growing, and the material will break.

In order to be able to talk about crack length and stress at the same time, the **stress intensity K** is defined as:

$$K = \sigma\sqrt{\pi c} \text{ [Pa}\cdot\text{m}^{1/2}]$$

To combine the material properties E and γ in one number, the critical stress intensity factor or **fracture toughness K_{1C}** is defined as:

$$K_{1C} = \sqrt{2\gamma E} \text{ [Pa}\cdot\text{m}^{1/2}]$$

As the name already suggests, K_{1C} is a measure for the toughness of a material, which is often used besides the area under the stress–strain curve.

The criterion for fracture is now very simple:

$$K > K_{1C}$$

Fracture can be due to a too high stress, or too long cracks, and the critical values can now be written as:

$$\sigma^* = \frac{K_{1C}}{\sqrt{\pi c}}$$

$$c^* = \frac{K_{1C}^2}{\pi \sigma^2}$$

These formulae are used mostly for the Griffith model, since we get some complications for metals, as is discussed in the next section. However, this form of the formulae is universally useful.

5.2.5 Ceramics vs. metals

As seen in Figure 5.14, growth of cracks in *ceramics* occurs by breaking bonds at the tip of the crack. All bonds have the ideal strength (as predicted by the Orowan model), and this is reached by stress concentration.

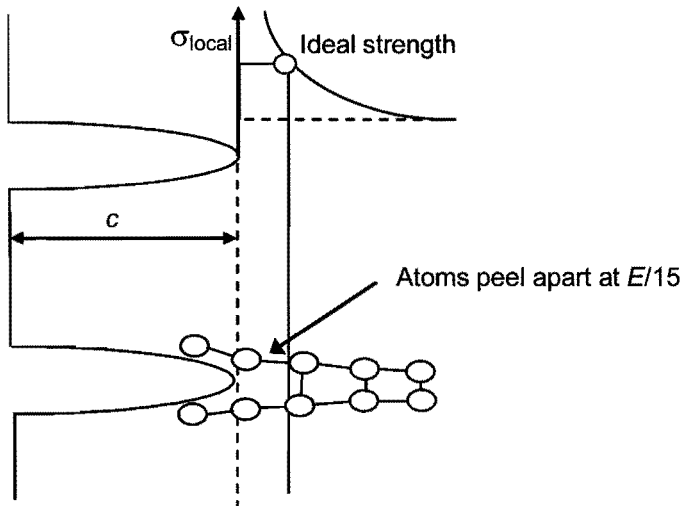


Figure 5.14. Growth of a crack in a ceramic must break atomic bonds.

Therefore, the value of K_{1C} is indeed as expected from the value of E and a surface energy of a few J/m^2 . Griffith's model works very well here:

$$K_{1C} = \sqrt{2\gamma E} \text{ [Pa}\cdot\text{m}^{1/2}\text{]}$$

Example: For Al_2O_3 we have $E = 390 \text{ GPa}$ and $K_{1C} = 3.7 \text{ MPa}\cdot\text{m}^{1/2}$. This gives $\gamma = 14,6 \text{ J/m}^2$. The tensile strength of Al_2O_3 is ca. 270 MPa , so there must be cracks with a maximum length of ca. $60 \mu\text{m}$.

For *metals*, K_{1C} is much higher than expected from the values of E and γ . Something is missing here from Griffith's model. The difference between metals and ceramics is that metals can show yield: plastic deformation, at much lower stresses than the stress needed for breaking metallic bonds. This plastic deformation absorbs a lot of energy because bonds have to be broken before they are formed again (see Figure 5.15). This means that the area around the crack can absorb more energy than expected from just crack growth. Therefore, it costs more energy to open up a surface than just the surface energy.

In metals the cracks grow by ductile tearing: the material is torn open, and a large area around the crack must be plastically deformed. Therefore, the yield strength is more important than the theoretical tensile strength. This behaviour can be incorporated in Griffith's model by substituting the **work of fracture** (W_f) for the surface energy γ :

$$K_{1C} = \sqrt{2EW_f}$$

For ceramics we find that $W_f = \gamma$, but for metals we have $W_f \gg \gamma$.

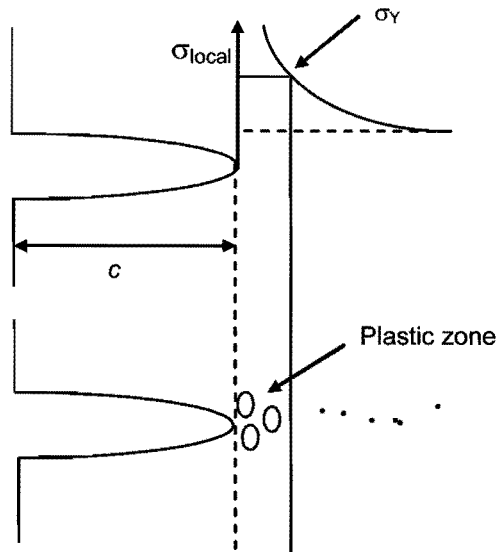


Figure 5.15. In metals, there is plastic distortion at the tip of a growing crack before bonds break.

Intermezzo

Be careful: $2W_f$ is sometimes referred to as G_c , the critical strain energy release rate, or just toughness. This last term is very confusing, since toughness is already used for K_{1C} itself. In Chapter 2, the normalized toughness that is plotted is G_c/ρ in Jm/kg. Other books simply give γ another value, without saying that it is no longer just the surface energy. And other books talk about $\gamma_c + \gamma_p$, where the first term is the surface energy, while the second term includes all energy necessary for plastic deformation.

Example: For aluminium we find $E = 72 \text{ GPa}$, and $K_{1C} = 45 \text{ MPa}\cdot\text{m}^{1/2}$. This leads to $W_f = 14 \text{ kJ/m}^2$. This is indeed much larger than the few J/m^2 that are expected for γ .

As has been mentioned before, the ductility of metals is due to the high mobility of dislocations. When a metal is sheared, ca. 10^{16} dislocations are formed per m^2 . Since each dislocation has an energy of ca. 10^{-9} J/m , this means that ca. 10^7 J/m^3 is necessary for creating the dislocations. When an area with a thickness of 1 cm around a fracture has to be deformed, this results in a work of fracture of ca. 10^5 J/m^2 . This is in good agreement with the numbers found from the fracture toughness.

Of course, the toughness is dependent on the temperature, as is the yield strength. In Figure 5.16, we can see the dependence for stainless steel.

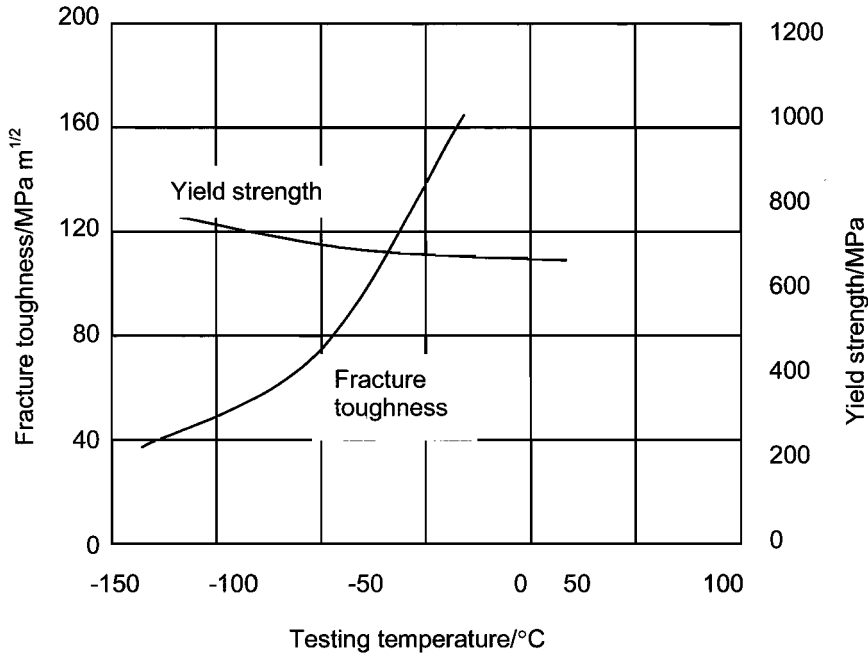


Figure 5.16. The mechanical properties of a metal depend strongly on the temperature.

Intermezzo

Fatigue

When a material is stressed and released repeatedly, or stressed periodically, there will also be fracture after a certain time, because plastic deformation occurs that leads to crack growth until c^* is reached. We will not look at this in detail here.

5.2.6 Overview

For inorganic materials, there are several relations between structure and mechanical properties on micro-, meso- and macro-level. They are given schematically in Figure 5.17. Ceramics will always show brittle fracture, and metals can undergo both ductile and brittle fracture, depending on whether σ_T or σ^* is the lowest value.

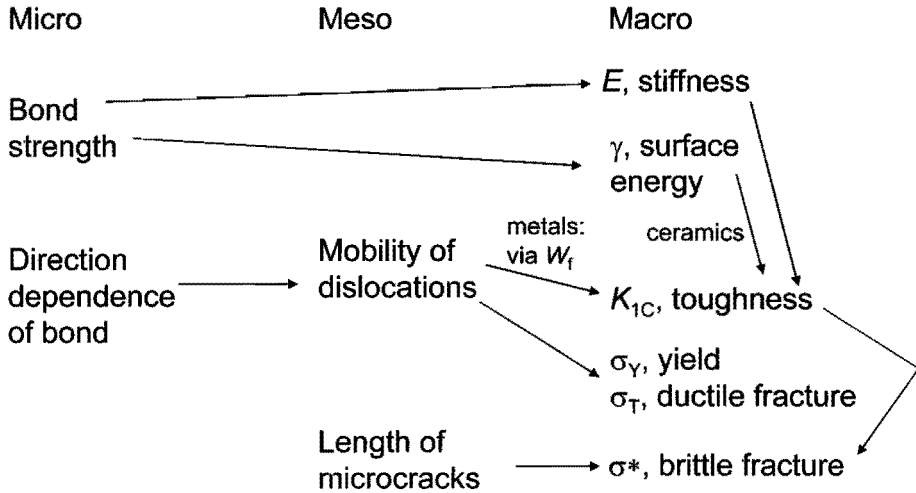


Figure 5.17. Relations between micro, meso and macro in inorganic materials.

5.3 Glasses

Glasses are inorganic materials without crystalline order.

Yield in glasses is caused mostly by viscous flow: the atomic bonds are broken and reformed in a random manner, causing plastic deformation. The bonds in glasses are as strong as in crystalline ceramics, so yield is difficult and most glasses break before they yield (at least, at low temperatures).

Fracture in glasses follows the same mechanisms as in crystalline solids: it is determined by the Griffith model with the growth of small cracks and a fracture toughness, which is low for ceramic glasses. So, glasses are not very tough.

Problems

- 5.1. A single crystal of Mo, shaped as a cylindrical rod with a 1 cm^2 cross section, is pulled in tension. If the crystal axis lies along the $[123]$ direction, at what applied load will crystal slip occur on the (110) plane in the $[1\bar{1}1]$ direction?
- 5.2. A copper sphere weighs 10 g. The surface energy of copper is 1.4 J/m^2 .
- Calculate the energy of the total surface of the sphere.
 - When the original sphere is broken down into fine spherical grains, each 100 nm in diameter, what is then the energy of the total surface?
- 5.3. When liquid mercury (Hg) is put on glass, drops are formed with a contact angle of 140° . It is known that the surface energy of Hg is 0.47 J/m^2 , and that of glass is 0.30 J/m^2 .
- Calculate the surface tension between glass and Hg.
 - Calculate the cohesion of both glass and Hg, and explain the difference via the type of chemical bonds.
 - Calculate the adhesion between Hg and glass, and the spreading coefficient of Hg on glass.
- 5.4.a. A steel with a yield stress of 1000 MPa contains a circular surface crack. What stress can be safely applied without deformation occurring near the crack?
- b. In the same steel an elliptical surface crack has a radius of curvature equal to 0.5 mm. How deep a crack can be tolerated without plastic deformation if the applied stress is 240 MPa?
- 5.5. A plate of steel has a yield stress of 1000 MPa. The plate fractured when the tensile stress reached 800 MPa, and it was hypothesized that a surface crack is present. If the fracture toughness for this steel is $60 \text{ MPa}\cdot\text{m}^{1/2}$, approximately what size of crack must be present?
- 5.6. Soda-lime glass has a surface energy of 0.30 J/m^2 and a Young's modulus of 69 GPa. Compute the critical stress required for the propagation of a surface crack of length 0.05 mm.
- 5.7. A specimen of a 4340 steel alloy with $K_{1C} = 45 \text{ MPa}\cdot\text{m}^{1/2}$ is exposed to a stress of 1 GPa. Will this specimen experience fracture if it is known that the largest surface crack is 0.75 mm long? Why or why not?
- 5.8.a. Compute the crack tip radius for an Al_2O_3 specimen that experiences tensile fracture at an applied stress of 275 MPa. Assume a critical surface crack length of 0.002 mm and a theoretical fracture strength of $E/10$.
- b. What critical fracture stress do you expect for this fracture length based on the Griffith model?

5.9.* A certain type of stabilized zirconia (ZrO_2) is evaluated as biomaterial. The supplier tells us there are internal defects with a length of 0.26 mm, and that $K_{1C} = 12 \text{ MPa}\cdot\text{m}^{1/2}$. The Young's modulus of ZrO_2 is 200 GPa.

- Calculate the maximum stress this material can stand in a tensile test.
- What surface tension can you calculate for this material? Is this an expected value? If not, what might explain the deviation?
- Explain why the supplier did not give us information about yield in this material.

5.10.* Stainless steel (type 304, annealed) is subjected to a tensile test.

- Calculate the maximum engineering stress this material can withstand. Carefully explain all assumptions.
- What is the maximum elastic strain for this material? Explain why it is so much smaller than the maximum engineering strain.
- Explain why this material has such a high ductility.

5.11.* A silicon (Si) single crystal is subjected to tensile stress in the $[2\bar{3}1]$ direction. What percentage of this stress will be a shear stress in the crystal?

5.12.* A single crystal of chromium (Cr) is stretched in the $[120]$ or $[0\bar{1}1]$ direction until plastic deformation occurs. Along which direction can the material withstand a higher force?

6 Organic Materials I: Structure of (bio)polymers

Organic materials are built up from very large molecules, with only weak bonds between them. Therefore, the materials are mostly amorphous, and the molecules are randomly coiled. We can then describe the structure of the material with a statistical distribution.

When we deform these materials, changing the shape and orientation of the macromolecules is very important.

I cannot teach anybody anything, I can only make them think.

Σωκράτης (Socrates)
(469–399 BCE)

6.1 Overview

6.1.1 Linear polymers and networks

There are various types of polymers as far as their chemistry is concerned. We will only briefly summarize this here; an overview of polymer structures can be found in Appendix I.

Macromolecules are formed by **polymerization** reactions, of which radical polymerization and polycondensation are the most important ones.

Radical polymerization leads to C–C bonds, and with the usual monomer $\text{CH}_2=\text{CHR}$, we get as structure for the macromolecule: $-(\text{CH}_2-\text{CHR})_n-$. Also, other structures are used, such as $-(\text{CH}_2-\text{CR}'\text{R}'')_n-$.

Examples:

R = H: poly(ethene), or poly(ethylene), PE

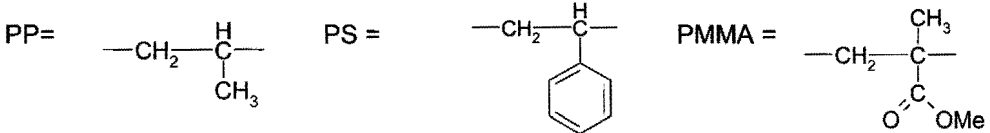
R = CH_3 : poly(propene), or poly(propylene), PP

R = C_6H_5 : poly(styrene), PS

R = Cl: poly(vinyl chloride), PVC

R' = CH_3 , R'' = COOCH_3 : poly(methyl methacrylate), Plexiglass, PMMA

$-(\text{CF}_2-\text{CF}_2)-$, poly(tetrafluorethene), Teflon, PTFE



Polycondensation leads to the formation of esters, amides and other bonds. The monomers must contain functional groups, such as carboxylic acids, alcohols, amines, etc.

Examples:

$-(\text{NH}-\text{R}-\text{CO})_n-$, nylons or poly(amide)s

$-(\text{O}-\text{R}-\text{CO})_n-$, poly(ester)s

$-(\text{O}-\text{R}-\text{NH}-\text{CO})_n-$, poly(urea)s

$-(\text{O}-\text{R}-\text{O}-\text{CO})_n-$, poly(carbonate)s

When different monomers are mixed, we get **copolymers**. Based on the sequence of the monomers, we get different types, as shown in Figure 6.1.

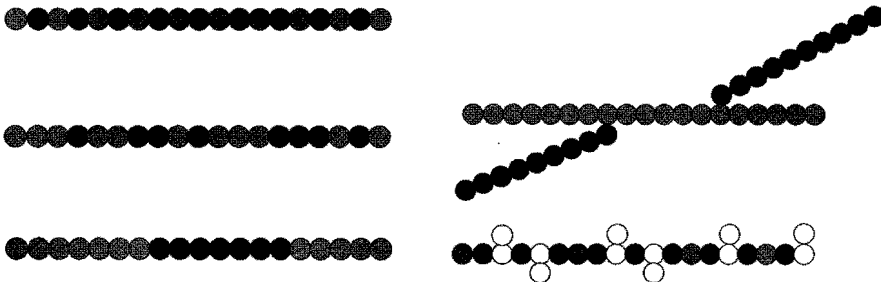


Figure 6.1. Copolymers can be alternating, random, and block (left, top to bottom); other types are graft copolymers and terpolymers (right).

The properties of polymeric materials can be tuned by changing the mixture of monomers.

For many polymers, there are different forms based on the stereochemistry of the carbon atoms in the different units: the configuration can be the same in all units (**isotactic**, see Figure 6.2 left), it can alternate in subsequent units (**syndiotactic**, middle), or be completely random (**atactic**, right). This has important consequences for the way in which these polymers can form crystals.

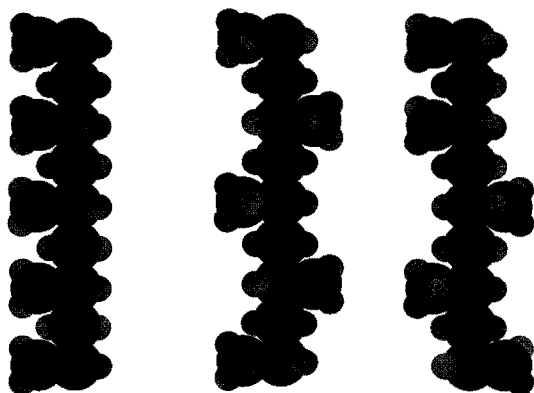


Figure 6.2. Different stereochemistries in polymer chains: isotactic (left), syndiotactic (middle), and atactic (right).

6.1.2 Modern architectures for polymers

Besides the standard linear polymers and networks there are nowadays also polymers with other topologies, each with specific properties. Branched polymers do not consist of a single linear molecule, but contain many places where the polymer chain branches. We have already seen the graft copolymers (see Figure 6.1). Other examples are: brush-, star-, and hyperbranched (arborescent) polymers, dendrimers, and LC (liquid crystalline) polymers (see Figure 6.3).

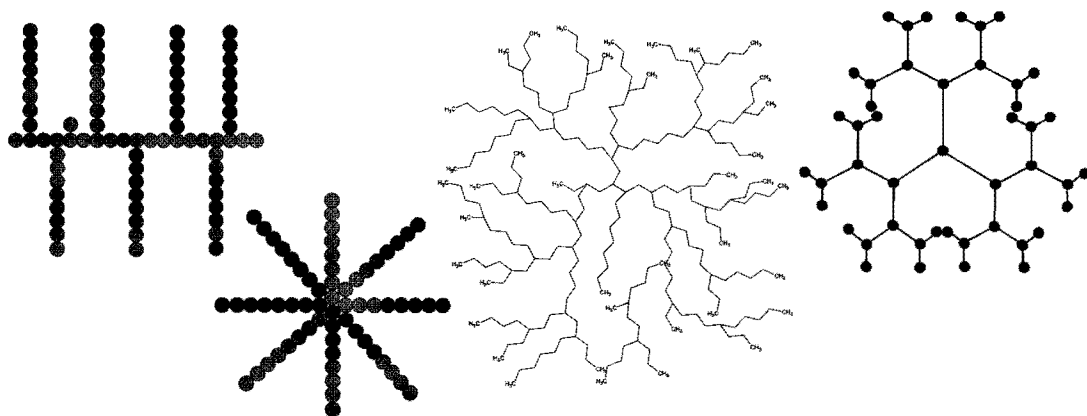


Figure 6.3. Polymer architectures: brush, star, hyperbranched, and dendritic.

6.1.3 Crosslink density

We are usually interested in the way in which the macromolecules are packed together to form a material. This can be influenced by covalent bonds between polymer chains (**crosslinks**), which lead to the formation of a **network**. This gives another way of classifying the polymers: the amount of crosslinks that are present.

Reversible **thermoplasts** are amorphous **coils** of macromolecules with possibly some crystalline areas (see Figure 6.4). There are (almost) no covalent crosslinks, so the material can be deformed irreversibly. However, at low temperatures the crystalline regions in the amorphous matrix can function as crosslinkers. And even for completely amorphous polymers at very high molar masses (very long molecules), there are **entanglements** between the molecules that can act as crosslinkers. But the crosslink density is low in all cases.

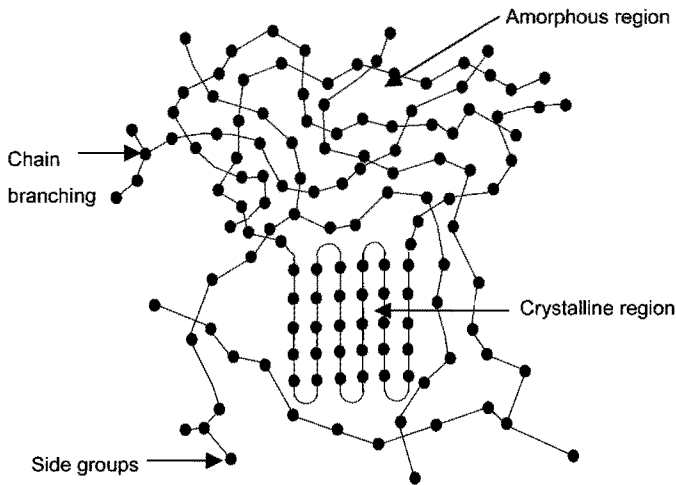


Figure 6.4. Typical structure of a thermoplastic polymer.

Examples: Non-crosslinked macromolecules, such as PE, PP, PVC, nylons.

Thermohardners are compact networks of covalent bonds between macromolecules, which are formed irreversibly, e.g. by heating or UV-irradiation (see Figure 6.5). Once formed, the network cannot change shape anymore. There is a very high crosslink density. These network compounds are often called **resins**.

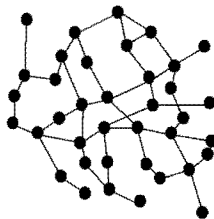
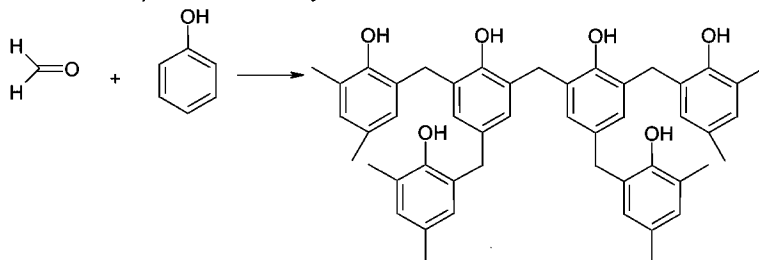


Figure 6.5. Typical structure for a thermohardener.

Examples:

- Network structures based e.g. on reaction between formaldehyde and phenol (Bakelite, see below), or formaldehyde and melamine:



- Epoxy resin, $-(O-Ph-C(CH_3)_2)-Ph-O-CH_2-CH(OH)-CH_2)_n-$, with compounds that connect the OH-groups (crosslinkers).

- Polyester resin, $-(CO-(CH_2)_m-CO-O-C(CH_2OH)_2)_n-$, also with crosslinkers.

Elastic **rubbers** or **elastomers** are networks with a small number of covalent bonds (see Figure 6.6), which are still elastic. The crosslink density is not very high.

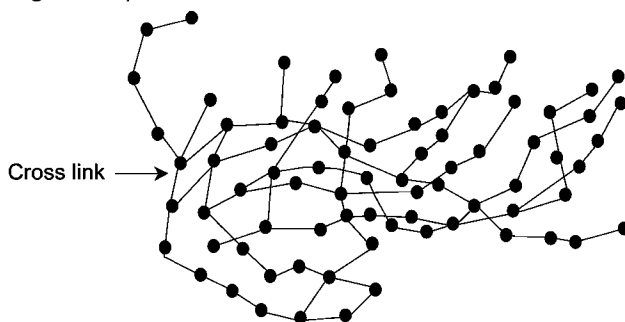


Figure 6.6. Typical structure for an elastomeric polymer.

Examples:

- SBR, styrene-butadiene rubber, copolymer $-(CH_2CHPh)_n-(CH_2-CH=CH-CH_2)_m-$, with crosslinks from e.g. sulphur between the C=C bonds.

- NBR, nitrile-butadiene rubber, copolymer $-(CH_2CHCN)_n-(CH_2-CH=CH-CH_2)_m-$, also with crosslinks from e.g. sulphur between the C=C bonds.

- Poly(isoprene), natural rubber, $-(CH_2-C(CH_3)=CH-CH_2)_n-$, crosslinked with sulphur

- Silicone rubber, $-(Si(CH_3)_2-O)_n-$, crosslinked via reactions with peroxides.

Intermezzo

Elastomers have high elasticity, but they can not be melted and shaped after synthesis. Thermoplasts can be melted, which has advantages for processing. Thermoplastic elastomers combine the properties because there are *reversible* crosslinks e.g. by ionic interactions or hydrogen bonding. At high temperatures these crosslinks can be opened, and the material can be processed. At low temperatures there is high strength and elasticity due to the crosslinks. An example is Lycra (Spandex), which contains many urea groups $(-NH-CO-NH-)$ that can form strong hydrogen bonds, while there are also long ethylene oxide chains $(-CH_2-CH_2-O-)_n$ that are very flexible.

6.1.4 Molar mass distribution

Most synthetic polymers are a mixture of macromolecules with different lengths, or **degrees of polymerization** (DP: number of monomers in the chain), and therefore different molar masses (also: molecular weight). In order to characterize the whole material, we need an average molar mass. This averaging can be done in two ways that both are important. It is determined by the way we describe the composition of the mixture of different macromolecules: with mole fractions or with mass fractions (sometimes, also volume fractions are used).

The **number-averaged molar mass** (M_n) is what we would normally consider the average: the molar masses of all macromolecules are added, and the total is divided by the number of molecules. If we have N_j mol of macromolecules with a length of j monomers (so DP = j), each with molar mass M_0 , we get a molar mass $M_j = jM_0$ for a macromolecule with length j .

The total number of macromolecules is:

$$N = \sum N_j \text{ [mol]}$$

We can now define the mole fraction of each macromolecule with a specific length j :

$$x_j = \frac{N_j}{N}$$

Then, the number-averaged molar mass is given by:

$$M_n = \frac{\sum(N_j M_j)}{N} = \sum(x_j M_j) = M_0 \sum(j x_j) \text{ [kg/mol]}$$

We can also look at the average degree of polymerization: for one chain it holds that DP = j , and for a mixture of chains we can define a number-averaged degree of polymerization (the average length):

$$DP_n = \sum(j x_j) = M_n / M_0$$

This is the most often occurring molar mass based on *molar* percentages.

Another kind of average can be determined when we look at the mass of a polymer with a specific length, instead of the number of chains: this is the **weight-averaged molar mass** (M_w). There is for polymers of length j a mass present of $N_j M_j$ kg, and the total mass is the sum of all these masses, so the mass (or weight) fractions of the various types are:

$$w_j = \frac{N_j M_j}{\sum(N_j M_j)} = \frac{x_j M_j}{M_n} = \frac{j N_j}{\sum(j N_j)} = \frac{j x_j}{\sum(j x_j)}$$

Then we can define the weight-averaged molar mass:

$$M_w = \sum(w_j M_j) = \frac{\sum(x_j M_j^2)}{M_n} = M_0 \frac{\sum(j^2 N_j)}{\sum(j N_j)} = M_0 \frac{\sum(j^2 x_j)}{\sum(j x_j)} = \frac{\sum(N_j M_j^2)}{\sum(N_j M_j)} \text{ [kg/mol]}$$

This is the most often occurring molar mass based on *weight (mass)* percentages. We can also define a weight-averaged degree of polymerization:

$$DP_w = \sum(jw_j) = M_w/M_0$$

The **polydispersity** of the polymer mixture is now defined as:

$$D = \frac{M_w}{M_n} = \frac{\sum(x_j M_j^2)}{M_n^2} = \frac{\sum(w_j M_j)}{\sum(x_j M_j)} = \frac{\sum(j^2 x_j)}{(\sum(j x_j))^2}$$

The more D deviates from 1, the broader the distribution of molar masses is in the mixture, as shown in Figure 6.7.

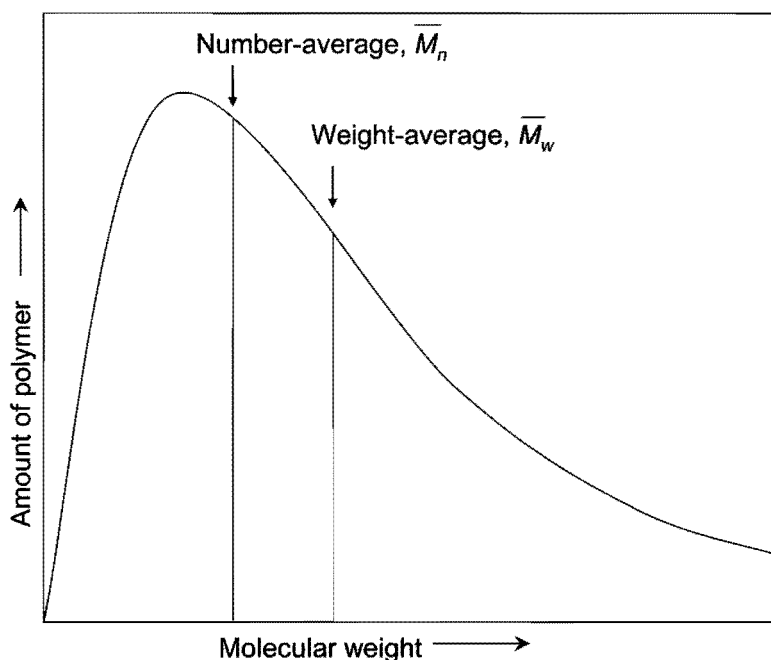


Figure 6.7. The two different averages for polymer molar mass. Sometimes M_n and M_w are given with an overbar, to indicate they are averages.

Example: Mix 20 g of a polymer with a molar mass of 20 kg/mol, 50 g with a molar mass of 100 kg/mol, and 30 g with a molar mass of 300 kg/mol. The total mass is then 100 g, so the mass fractions are: 0.2, 0.5 en 0.3. M_w can then be calculated to be 144 kg/mol.

The molar quantities follow from $N_j = m_j/M_j$, and are respectively 1 mmol, 0.5 mmol, and 0.1 mmol. Total amount: 1.6 mmol, so the mole fractions are: 10/16, 5/16 en 1/16. This gives: $M_n = 62.5$ kg/mol.


The polydispersity is then: $D = M_w/M_n = 2.3$.

6.1.5 Polymers as biomaterials

Polymers are often used in the human body as sutures, blood vessels, replacements for soft tissues (ear, nose, etc.), and in hip joints. Examples are:

- poly(ethylene) (PE, hip, tendon implant, facial implant);
- poly(ethylene terephthalate) (PET, aorta, tendon, facial implant)
= $-(\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{Ph}-\text{CO})_n-$;
- poly(methyl methacrylate) (PMMA, Plexiglas, intra-ocular lens, bone cement);
- poly(dimethylsiloxane) (PDMS, silicones, breast prostheses) = $-(\text{Si}(\text{CH}_3)_2-\text{O})_n-$;
- poly(urethanes) (PUR, skin and vessels) = $-(\text{O}-\text{R}-\text{O}-\text{CO}-\text{NH}-\text{Ar}-\text{NH}-\text{CO})_n-$
(various R = alkyl and Ar = aromatic group).

As hydrophilic polymers one often sees:

- poly(ethylene oxide) (PEO = poly(ethylene glycol, PEG)
= $-(\text{CH}_2\text{CH}_2\text{O})_n-$;
- poly(N-vinylpyrrolidinone) (PNVP) = $-(\text{CH}_2\text{CHY})_n-$, with Y = 

Typical biodegradable polymers are:

- poly(lactic acid), PLA, $-(\text{O}-\text{CH}(\text{CH}_3)-\text{CO})_n-$;
- poly(glycolic acid), PGA, $-(\text{O}-\text{CH}_2-\text{CO})_n-$.

Polymers are easy to produce and are flexible, but they can change shape after some time, and they can degrade in a biological environment. For many polymers, this last property is actually an advantage, since they will then disappear from the body after a while, when their function is finished. In joints, polymers can sometimes produce particles by friction, which can lead to inflammation.

Some polymers must be modified on the surface in order to become biocompatible or bioinert. Apolar polymers can be treated with e.g. a plasma to get a more polar surface. Also, a more polar hydrophilic polymer (e.g. PEO) can be attached to the surface (graft copolymer).

The surface properties are again related to the surface energy γ , which can be determined by measurements of the contact angle with e.g. water ($\gamma = 72.8 \text{ mJ/m}^2$ versus air). The more polar the surface is, the higher γ_{SG} is, and the lower γ_{SL} then is (see Table 6.1). These values are e.g. of importance when trying to predict whether proteins will attach to the polymer surface or not.

Table 6.1. Contact angles and surface tensions of various polymers vs. water.

Material	$\theta(\text{H}_2\text{O})$	$\gamma_{\text{SG}} (\text{mJ/m}^2)$	$\gamma_{\text{SL}} (\text{mJ/m}^2)$
nylon-6	61°	46.6	10.8
nylon-6,6	70°	41.1	16.8
PET	79°	36.0	22.2
PS	84°	32.4	24.8
PE	87°	30.3	26.6
PTFE	104°	20.0	37.6

6.2 Morphology: crystalline/amorphous

6.2.1 Polymer crystals

In the case of polymers, the molecules are much larger than the unit cells of crystal lattices, so we can only talk about the crystallization of segments of the polymer chain. The chain must then fold up to form a regular crystal structure, and we get **lamellar** shapes of 10–20 nm thickness (see Figure 6.8). These lamellae can form so-called **spherulites**.

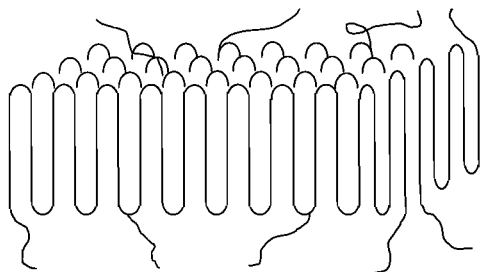


Figure 6.8. Polymer crystals are platelets with dangling molecules, formed by folded chains.

A polymer can almost never be 100% crystalline, so there is always an amorphous part, and we have semi-crystalline materials. A polymer can normally only crystallize when the structure of the chain is regular (iso- or syndiotactic). Atactic polymers are almost always amorphous.

Biopolymers can also crystallize, although this does not happen a lot in a living organism. Artificial proteins with certain repeating amino-acid sequences can form lamellar crystals, because β -sheets are formed between chains with a Gly–Ala repeating unit, while a Gly–Glu pair creates a hairpin turn.

The molar mass (and molar mass distribution) and the percentage crystalline state determine how the polymer behaves, as shown in Figure 6.9.

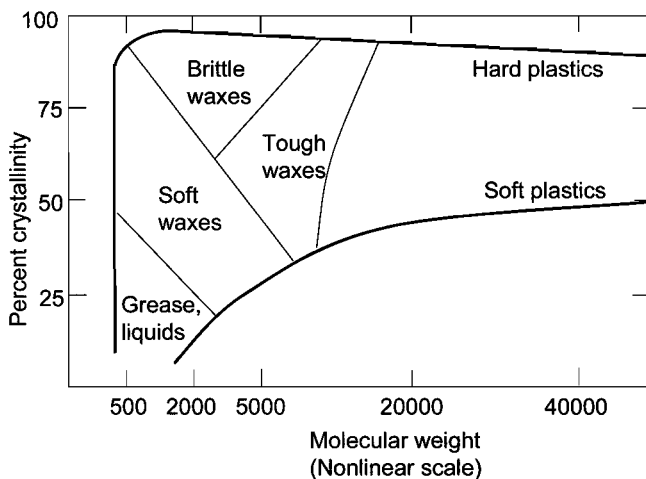


Figure 6.9. Dependence of behaviour on molar mass and crystallinity.

6.2.2 Glass transition

As we have seen before for inorganic glasses, amorphous polymers also show a glass transition. This glass transition temperature (T_g) is the temperature where segments of the polymer chain start to move, and it is determined by:

- chain flexibility, interactions between chains, and crosslinking; less flexibility gives a higher T_g

- chain length, or molar mass: $T_g = T_{g,\infty} - \frac{C_T}{M_n}$

- the time scale of the measurement; faster measurement: higher T_g .

The cooling rate can then lead to more or less **free volume** in a V, T -diagram (see Figure 6.10): this is the volume difference between the expected volume of the glass above the T_g and the actual behaviour as a melt.

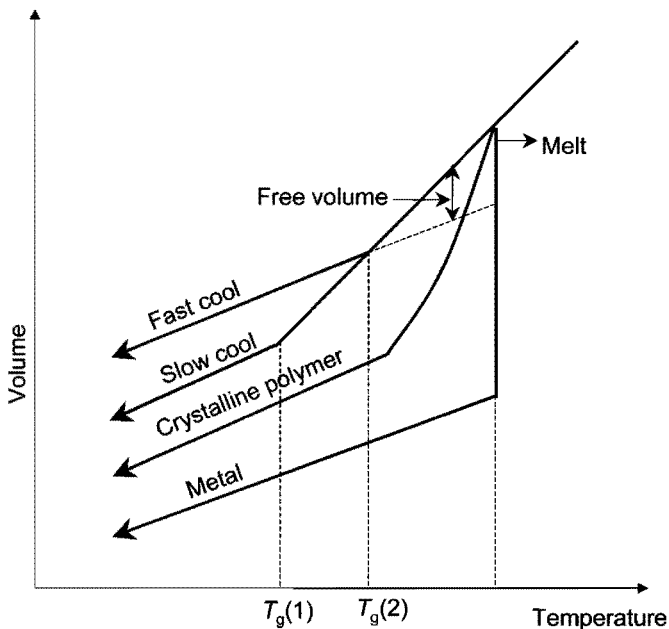


Figure 6.10. The glass temperature is dependent on the speed of the measurement, and is typical for the non-crystalline thermoplasts.

This behaviour is of course typical for the thermoplasts, which have a large amorphous part. Thermohardners are non-crystalline materials, but they do not show a glass transition, because the many crosslinks prevent motion of the main chain. A rubber (elastomer) below its T_g is a glass, with van der Waals bonds besides the covalent crosslinks. Above T_g a rubber is in fact a viscous liquid, which is kept together by a few covalent crosslinks.

Besides a glass transition temperature (T_g) a polymer can also have a melting temperature (T_m) for its crystalline state. Together with the molar mass, the temperature will influence the mechanical properties of the polymeric material, as shown in Figure 6.11.

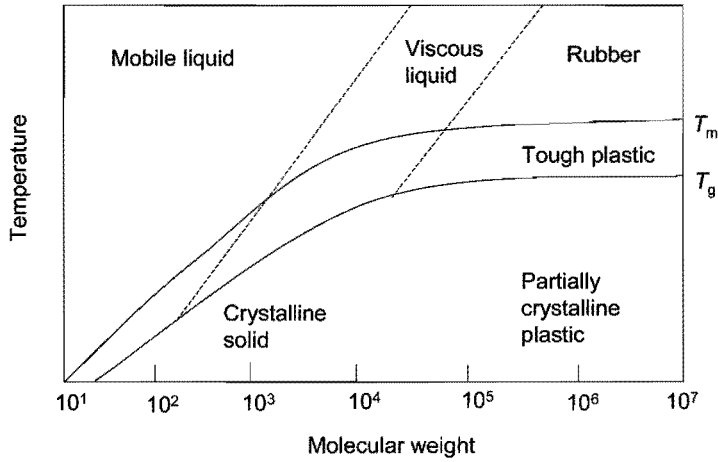


Figure 6.11. Both molar mass and temperature influence the mechanical behaviour of polymers.

For various polymers the glass temperature T_g and the melting temperature T_m follow the same trend (see Figure 6.12).

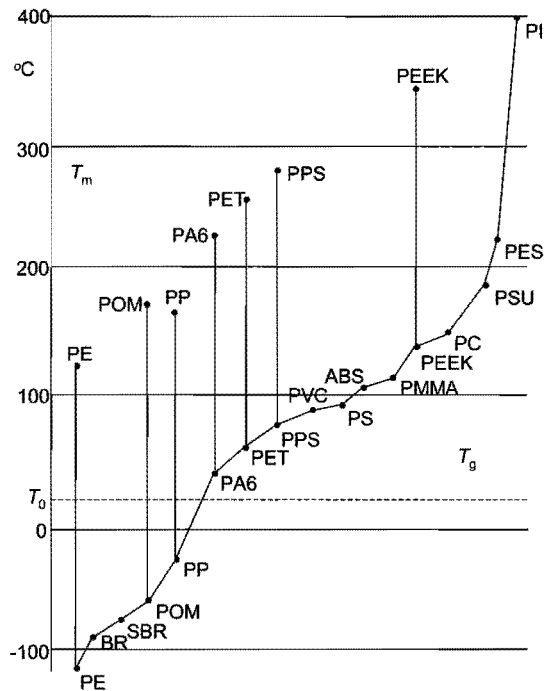


Figure 6.12. Trends in T_g and T_m for various polymers.

6.2.3 Random-coil model for the amorphous state

In order to describe how an amorphous polymer behaves, we need to know something about its dimensions. For a polymer that is randomly distributed in space, we can set one end at the origin. The distance to the other chain end can then be called the end-to-end distance r_c (see Figure 6.13).

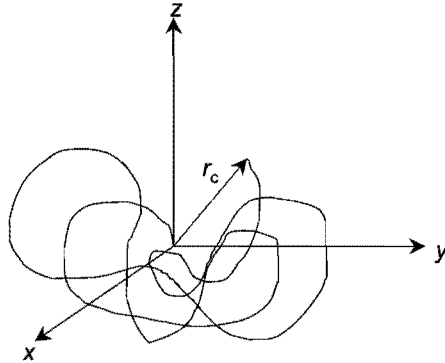


Figure 6.13. The random coil of a polymer chain with the end-to-end distance indicated.

There is a statistical model (the **random-coil model**) that is now very useful. This model is also known as the random walk, and it is easiest to first look at it in one dimension: suppose you start on a line at position 0 and you can make random steps to the left or the right of length L . Then your position after one step will be:

$$R_1 = \pm L$$

In order to get rid of the unknown sign, we will use the square of the distance:

$$R_1^2 = L^2$$

Now for step N , we can write:

$$R_N = R_{N-1} + L, \text{ or } R_N = R_{N-1} - L$$

Again we use the trick with the square:

$$R_N^2 = R_{N-1}^2 \pm 2R_{N-1}L + L^2$$

On average, there are as many steps to the left as to the right, so:

$$\langle \pm 2R_{N-1}L \rangle = 0$$

(where the $\langle \rangle$ brackets stand for the average value) and we are left with:

$$\langle R_N^2 \rangle = \langle R_{N-1}^2 \rangle + L^2 \quad (\text{of course, } \langle L^2 \rangle = L^2, \text{ as it is a constant})$$

If you now look back at the starting value of $\langle R_1^2 \rangle (= R_1^2)$, you can easily see that we always will get for the so-called **root-mean-square value** of the distance:

$$\langle R_N^2 \rangle = NL^2$$

Amazingly, this is also true when we switch to three dimensions (see Appendix N).

If the polymer chain consists of n_s segments, each with length L_s , then the average radius of the polymer coil is:

$$\sqrt{\langle r_c^2 \rangle} = L_s \sqrt{n_s} \quad [\text{m}]$$

Another average radius that is used a lot (based on the distance to the centre of mass) is the **radius of gyration**, R_g . It is obtained from experimental techniques like light scattering, and for a random coil it can be shown that:

$$R_g^2 = \frac{\langle r_c^2 \rangle}{6} \quad [\text{m}^2]$$

so:

$$R_g = L_s \sqrt{\frac{n_s}{6}} \quad [\text{m}]$$

For real macromolecules, a completely random distribution over space is of course not possible: the bonds have specific angles θ (according to the VSEPR theory), and there are preferences for certain conformations (staggered) with specific torsional angles ϕ . This leads to the expression:

$$\langle r_c^2 \rangle = C_r n_s L_s^2 = n_s L_s^2 \frac{1 - \cos \theta}{1 + \cos \theta} \times \frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle}$$

where C_r has a value between 5 and 10, e.g. 6.7 for poly(ethylene), and 10 for poly(styrene). The θ -factor is 2 for the common angle $\theta = 109.5^\circ$ (tetrahedral). The ϕ -factor is often called σ_r^2 , where σ_r varies between 1.5 and 2.5. σ_r is then referred to as the characteristic radius of the polymer, and is indicative of the stiffness of the polymer chain.

Intermezzo

Better theoretical models predict $\langle r_c^2 \rangle \sim n_s^{3/5}$, and numerical simulations also suggest $\langle r_c^2 \rangle \sim n_s^{0.6}$, so there are more possibilities to change the formula.

For polymers in solution there can also be an interaction with the solvent, which usually swells the coil, but can also shrink it. Only at a certain temperature for each solvent, the θ -condition, the formula for $\langle r_c^2 \rangle$ also holds in solution.

6.2.4 Implications for the amorphous state

Suppose we have a poly(ethylene) (PE) with a molar mass of 280 kg/mol, and therefore a degree of polymerization (length as number of monomer units) $n_s = 10^4$. For this molecule we then have: $L_s = 0.154 \text{ nm}$ and $C_r = 6.7$, so $\langle r_c^2 \rangle = 1590 \text{ nm}^2$. Then the average distance between the chain ends is 40 nm, and the radius of gyration: $R_g \approx 16 \text{ nm}$.

The volume of this random coil is now $V = \frac{4\pi}{3} \langle r_c^2 \rangle^{3/2} = 2.66 \times 10^{-22} \text{ m}^3$. The mass of 1 chain follows from the molar mass: $4.67 \times 10^{-22} \text{ kg}$. This gives a density of one polymer coil of 1.75 kg/m^3 .

In reality PE has a density of 855 kg/m^3 , so the polymer coils do not lie next to each other in the material, but are highly entangled. This is very important for the mechanical properties, because the long chains can only move past each other with difficulty due to the entanglements.

If we try to stretch a polymer chain completely, then the distance between the chain ends can in theory be $r_c = n_s L_s$, which leads to an elongation:

$$\lambda = 1 + \varepsilon = \frac{n_s L_s}{\sqrt{\langle r_c^2 \rangle}} = \sqrt{\frac{n_s}{C_r}}$$

For the PE we used in the previous example, we then get: $\lambda = 38.6$. So, a polymer can be stretched very much when the chains are uncoiled, as shown in Figure 6.14.

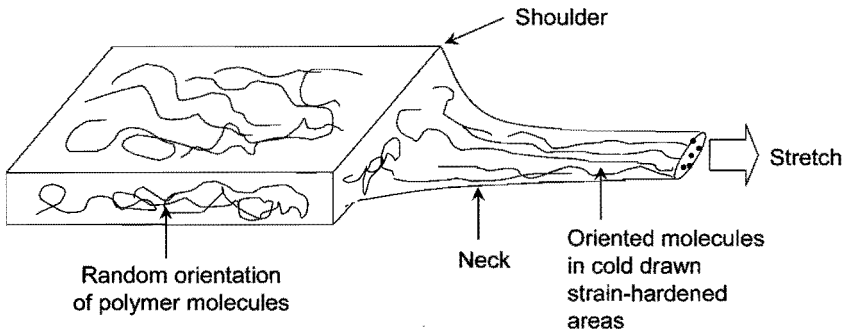
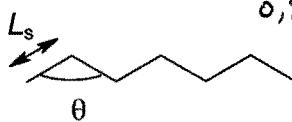


Figure 6.14. The effect of stretching a polymeric material.






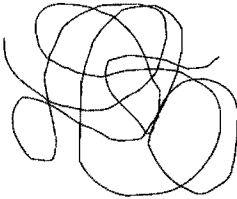
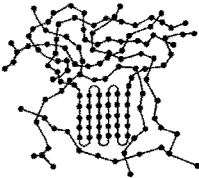

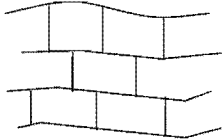
In reality, λ will be lower, since most bonds cannot be stretched to be completely straight. A polymer chain with C–C bonds will e.g. have angles of $\theta = 109.5^\circ$, and the maximum length will be: $r_c = n_s L_s \sin(\theta/2) = 0.817 n_s L_s$, instead of $n_s L_s$.



Besides the entanglements between the polymer chains, there are of course also the normal intermolecular interactions: always van der Waals forces, sometimes dipole–dipole interactions or hydrogen bonds. These can also change the shape and behaviour of the coils.

6.2.5 Overview

Below, an overview is given of the various structural elements that we find in synthetic polymers on the micro and meso level.

Micro		
Atactic 	Isotactic 	Syndiotactic 
Linear 	Branched 	Tangled 
Meso		
Partially crystalline 	Lightly cross-linked 	Close network 

6.3 Biopolymers

We will look at proteins, polysaccharides and poly(hydroxyalkanoates). All are built up from optically pure monomers (amino acids, sugars, and hydroxy-acids). Biopolymers usually have polydispersity $D = 1$, because they are constructed monomer by monomer. Of course, there can be different lengths for different purposes. Also, there are usually no random copolymers: the sequence is determined by the genetic program, executed by enzymes.

6.3.1 Proteins

Proteins are polymers of amino acids via amide bonds (the primary structure) that can fold in water to secondary structures (α -helix, β -sheet; via amide H-bonds), and tertiary structures (determined by hydrophobic interactions, H-bonds and electrostatic interactions, solidified by S–S bridges). In fact, proteins are polyamides like nylons. Because there are various side groups present (so proteins are copolymers), some people also speak of “decorated nylon”.

As far as structural proteins are concerned, we do not find the folded globular structures as in enzymes, but fibrillar structures. Often these fibres are crosslinked to form elastic networks. The best known examples of structural proteins are collagen, keratin, and spider dragline silk as typical strong fibres, and elastin as typical rubber.

Collagen is the most common protein fibre. There is a primary structure of ca. 1000 amino acids, where the triad Gly–X–Pro/Hyp is repeated. Hydroxyproline (Hyp) is a special form of proline with an OH-group added. This chain forms a 280-nm long left-handed helix. Three of these chains form a right-handed superhelix, and are kept together by hydrogen bonds and covalent crosslinks. This is called tropocollagen, with a molar mass of 285 kDa, a length of 300 nm, and a diameter of 1–5 nm.

Because there are several varieties of proteins that can be combined in the triple helix, we find different types of collagen. For example: type I is the most common one, in stretched tissues such as tendon, skin and bones; type II is found in connective tissues that are compressed, such as cartilage; type III is found in skin and blood vessels.

The further build-up follows a hierarchical pattern (see Figure 6.15): multiple tropocollagens combine in a microfibril, and these combine again to a subfibril. These form fibrils, which are grouped together in fascicles, and finally a tendon is formed.

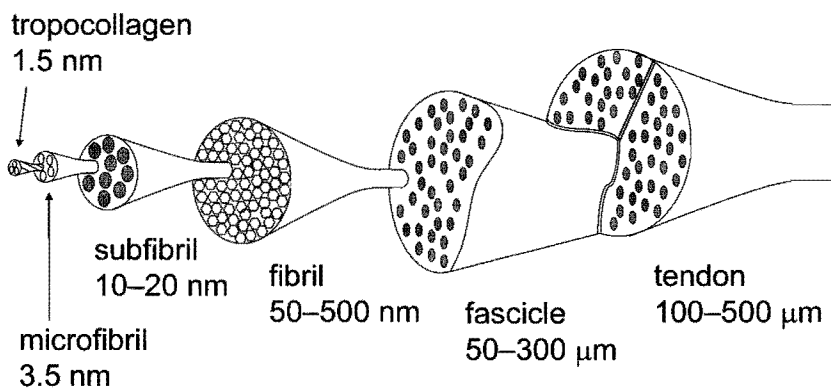


Figure 6.15. Hierarchical build-up of collagen in tendons.

Keratins are found in hair (also wool), nails and skin, and in animals also in horn, feathers and hoofs. The proteins have various amino-acid sequences, but there are always many S–S bridges. In the relaxed state there are many α -helices, but upon stretching these unfold to β -sheets.

Here also we find a hierarchical structure: the α -helices all have a repeating sequence of 7 amino acids (*a* to *g*), of which 2 are hydrophobic in nature (*a* and *d*). In a top view (see Figure 6.16), this works out as follows (from *a* to *g* the helix runs into the paper): the apolar amino acids *a* and *d* end up precisely next to each other on one side of the helix.

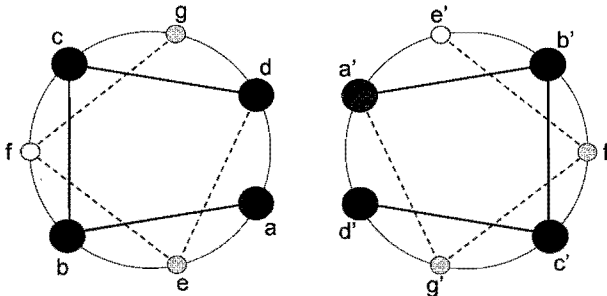


Figure 6.16. Top view of the α -helices in keratin.

This leads to a hydrophobic strip on the helix (see Figure 6.17), and two helices in water will now associate by attaching these strips to each other. This gives a so-called coiled-coil structure: a left-handed superhelix.

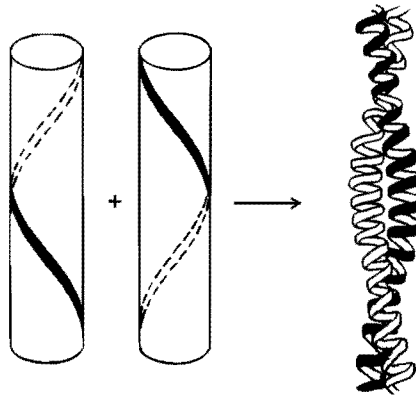


Figure 6.17. Two α -helices combine to a superhelix by hydrophobic interactions.

Two coiled coils now combine to a protofilament, and subsequently two protofilaments combine to a protofibril. When a total of 4 protofibrils coil around each other in a right-handed fashion, this is called a filament. Together with a matrix, this then forms a composite material: the microfibril. Many microfibrils form a macrofibril, which then cluster together to form a hair, in a similar hierarchical build-up as seen for tendon.

Silk consists of the protein fibroin, which forms β -sheets via hydrogen bonds. The amino acid sequence has as repeating unit the hexapeptide Ala–Gly–Ala–Gly–Ser–Gly, in which a **small and a large amino-acid side chain alternate**. Because of this structure, two fibroin chains can fit together like a zipper, as seen in Figure 6.18.

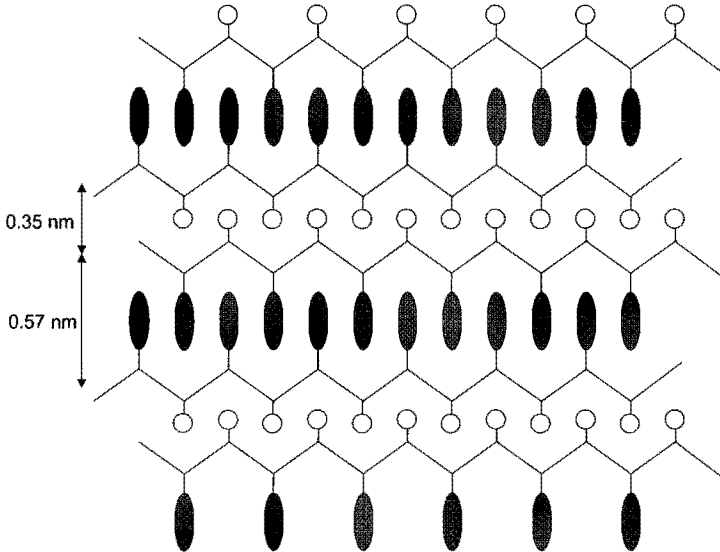


Figure 6.18. β -Sheets of fibroin where the small amino acids (Gly) and the large amino acids (Ala or Ser) fit together.

The protein is semi-crystalline, so there are small crystalline areas in an amorphous matrix. With this material, the dragline of a spider web is constructed. It is very important to realize that the silk fibres are spun by the spider, which directly gives a preferred orientation to the fibres. This trick can now be duplicated by chemists for synthetic polymers.

Elastin is a protein that is the typical bio-rubber: it is very elastic. It leads to tissues with a yellow colour, such as the elastic cartilage in the ear and blood vessel walls. During aging, calcium phosphate crystallizes on the elastin fibres, and the tissues become less elastic: e.g. skin starts to wrinkle.

Elastin consists for 55–70% of the repeating sequence Gly–Ala–Ser. Most of these amino acids (60%) are apolar, and many β -turns occur. Therefore, helices are formed, which can unwind upon stretching. There are fibres with a diameter of 5.5 nm and a length of 5–7 μm . The protein has many intermolecular crosslinks (particularly via lysine side groups), and therefore is a typical rubber (see Figure 6.19).

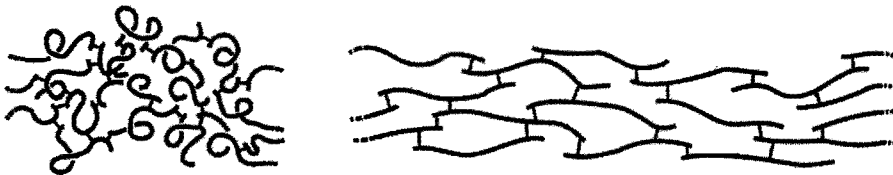
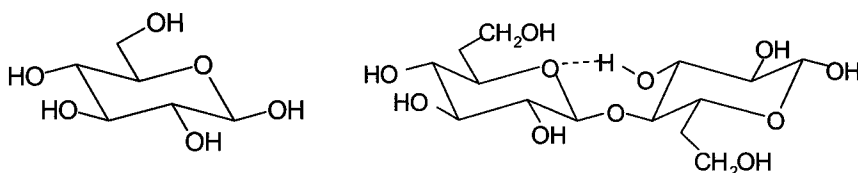


Figure 6.19. Elastin can be reversibly stretched due to its many crosslinks. Left shows the molecules in rest, right shows the stressed form.

6.3.2 Polysaccharides

These are polyacetals, and they are found in many forms: in humans we know glycogen, and in plants there is starch, but these are both storage polymers for glucose. As structural material only cellulose (in plants) and chitin (in insects) are of importance. In humans, we find many modified sugars, which can form gels in water: the hyaluronic acids. These are of importance mainly in composite biomaterials (see Chapter 9).

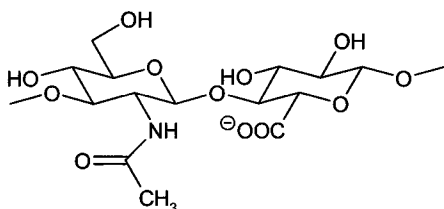
Cellulose is a polymer of glucose via 1,4-bonds. It is of importance that glucose only has the β -configuration in this polymer: this allows many H-bonds in the chain, which increases the strength of the material. With α -glucose we get glycogen, which is not a good structural material.



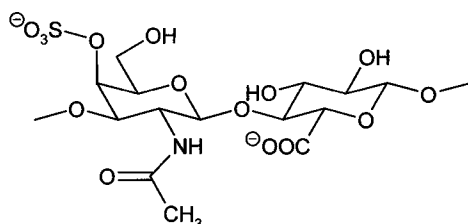
Cellulose forms fibrils with a diameter of 3.5 nm from ca. 40 molecules via H-bonds between the chains, and then combines the fibrils to larger fibrils (20–25 nm diameter). In fibres, these fibrils are wound in a specific angle, which is very important for the stiffness of the material.

Gels of polysaccharides are formed when the sugars are modified with acid groups, such as sulphonic acids or carboxylic acids. In water these will form poly-electrolytes, which are highly swollen with water, and can form networks. In humans, the most important examples are the **glycosaminoglycans (GAGs)**, long polymers that occur in five classes:

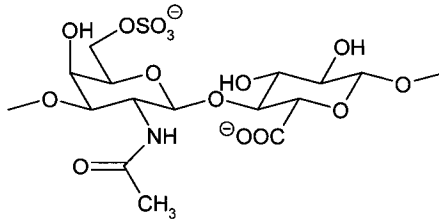
- Hyaluronic acid: repeat of *N*-acetyl- β -D-glucosamine and β -D-glucuronic acid. Occurs in skin, cornea, heart valves, and synovial fluid.



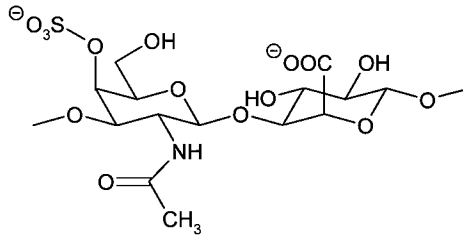
- Chondroitin-4-sulphate: repeat of *N*-acetyl- β -D-galactosamine-4-sulphate and β -D-glucuronic acid. Occurs in cartilage, skin, and cornea.



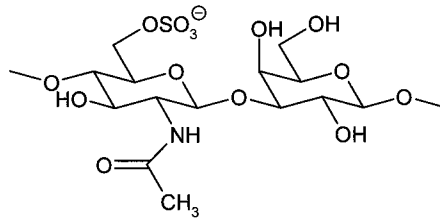
- Chondroitin-6-sulphate: repeat of *N*-acetyl- β -D-galactosamine-6-sulphate and β -D-glucuronic acid. Occurs in cartilage, tendon, and intervertebral discs.



- Dermatan sulphate: repeat of *N*-acetyl- β -D-galactosamine-4-sulphate and β -L-iduronic acid. Occurs in skin, tendon, ligaments, and heart valves.

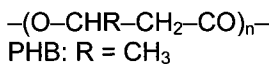


- Keratan sulphate: repeat of *N*-acetyl- β -D-glucosamine-6-sulphate and β -D-galactose. Occurs in cartilage, cornea, and intervertebral discs.



6.3.3 Poly(hydroxyalkanoate)s (PHAs)

These are isotactic polymers made by bacteria, which use them for energy storage. They can form up to 80% of the dry cell mass, and are therefore quite easy to isolate. The most common one is poly(D-3-hydroxybutyrate) (PHB).



PHB is rather stiff and brittle, but this can be improved by adding propanoic acid to the nourishment of the bacteria. This leads to the formation of a copolymer of hydroxybutanoic acid (hydroxybutyrate) and hydroxypentanoic acid (hydroxyvalerate) with better mechanical properties.

Problems

- 6.1. What is the difference between configurations and conformations in polymer chains?
- 6.2. What is the degree of polymerization of a poly(styrene) sample that has a number-averaged molar mass of 129 kg/mol?
- 6.3. If the degree of polymerization of poly(vinyl chloride) is 729, what is then the molar mass of the polymer?
- 6.4. A copolymer of vinyl chloride and vinyl acetate ($C_4H_6O_2$) contains a ratio of 19 parts of the former to 1 part of the latter. If the number average molar mass is 21 kg/mol, what is the degree of polymerization?
- 6.5. A certain rubber is composed of equal weights of isoprene ($C_4H_5CH_3$) and butadiene (C_4H_6).
- What is the mole fraction of each of the rubber components?
 - How many grams of sulphur must be added to 2 kg of this rubber to crosslink 1% of all the repeating units? *Note:* 1 S atom crosslinks 2 repeating units.
- 6.6. A PP polymer contains equal numbers of macromolecules with 450, 500, 550, 600, 650, and 700 repeating units. What is the average molar mass by number and by weight?
- 6.7. Below, molar mass data for a poly(propene) material are tabulated. Compute:
- The number-averaged molar mass.
 - The weight-averaged molar mass.
 - The number-averaged degree of polymerization.
 - The weight-averaged degree of polymerization.
 - The polydispersity.

Molar mass [kg/mol]	mole fraction	mass fraction
8–16	0.05	0.02
16–24	0.16	0.10
24–32	0.24	0.20
32–40	0.28	0.30
40–48	0.20	0.27
48–56	0.07	0.11

6.8. Poly(ethylene) (PE) has a density of 1000 kg/m^3 in crystalline form, and a density of 865 kg/m^3 in the amorphous state.

a. When a linear PE has a density of 970 kg/m^3 , what is then the mass fraction of crystalline polymer?

Hint: Start with 1 kg of polymer, and split it into crystalline and amorphous parts.

Call the crystal mass fraction x , and proceed from there.

b. A branched PE has a density of 917 kg/m^3 . What is the mass fraction of crystalline polymer in this material?

c. Why is the density of branched PE lower than that of linear PE?

6.9. In crystalline form a polymer melts at $240 \text{ }^\circ\text{C}$, but in amorphous form it has a glass transition at $90 \text{ }^\circ\text{C}$. The coefficient of thermal expansion of the liquid polymer is three times that of the solid polymer. If the polymer volume expands linearly with the temperature in both cases, what is the ratio of the free volume at $100 \text{ }^\circ\text{C}$ and at $200 \text{ }^\circ\text{C}$?

6.10. Give the reason why the glass transition temperature (T_g) differs for the following pairs of polymers with similar chemical composition and the same molar mass:

a. PE (150 K) vs. PP (250 K)

b. Poly(1-butene) (249 K) vs. poly(2-butene) (200 K)

c. PEO (232 K) vs. poly(vinyl alcohol) (358 K)

d. Poly(ethyl acrylate) (249 K) vs. PMMA (378 K)

6.11. A polypeptide can sometimes be treated as a random coil. If the length of an amino acid is 0.34 nm , what are then the average radius and the radius of gyration of a 100-amino-acid polypeptide?

6.12.* We have a polymer with $M_n = 9000 \text{ g/mol}$, and we wish to lower the T_g by lowering the average molar mass. For this polymer it is known that: $T_{g,\infty} = 164 \text{ }^\circ\text{C}$ and $C_T = 98866 \text{ }^\circ\text{C}\cdot\text{g/mol}$.

How many moles of the same polymer with $M_n = 100 \text{ g/mol}$ must be added to 1 mole of the original polymer to lower its T_g to $121 \text{ }^\circ\text{C}$?

7 Organic Materials II:

Mechanical properties of (bio)polymers

In this chapter we will apply the structural knowledge of organic materials to understanding their mechanical properties. Since these are quite different from the ones seen for inorganic materials, we will first give an overview of what to expect, and then treat each property in detail.

Compared to the inorganic materials, we now have very weak bonds between the molecules. That means that elastic and plastic deformation occur simultaneously: bonds are stretched so easily, that bond breaking and viscous flow (as for glasses) occur together. That is why we speak of visco-elastic behaviour.

Nothing is too wonderful to be true if it be consistent with the laws of nature,
and in such things as these, experiment is the best test of such consistency.

Michael Faraday
(1791–1867)

7.1 Overview

The mechanical properties of polymers are highly dependent on the temperature: polymers are **visco-elastic**, and can behave like glasses, rubbers (elastic deformation), or flow like viscous liquids. This viscous part absorbs energy, so the σ, ϵ -curves always show hysteresis (see Chapter 2).

Also, the strength and toughness are different for the glass and rubbery state: below the glass transition (T_g) there is brittle fracture like in ceramics, while above the T_g there is yield and plastic deformation as in metals (see Figure 7.1). The yield stress is therefore strongly dependent on temperature and the speed of the measurement (faster gives higher values for σ_Y).

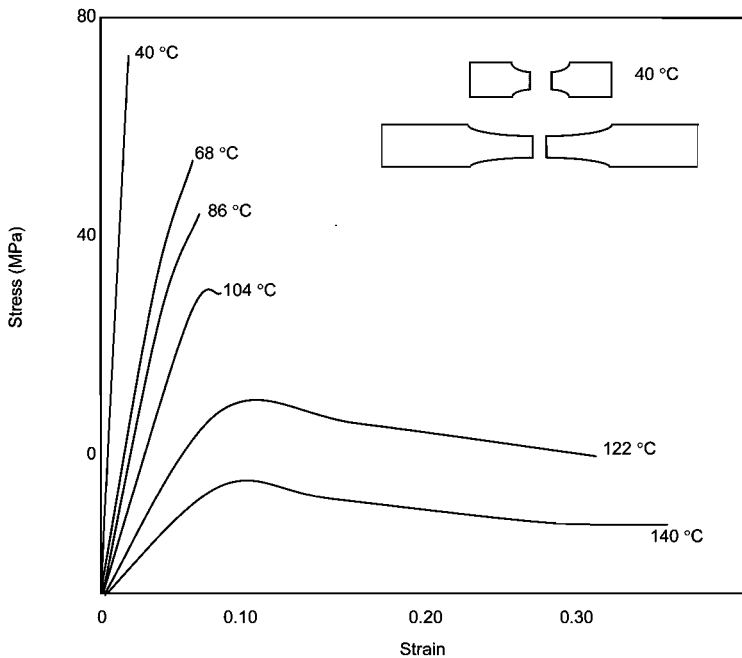


Figure 7.1. Mechanical properties of polymers are dependent on the temperature.

It is also very important always to consider what the structure of the polymer is: we can have highly crystalline materials, glasses, semi-crystalline materials and rubbers (elastomers). These all have different mechanical properties, as shown in Figure 7.2.

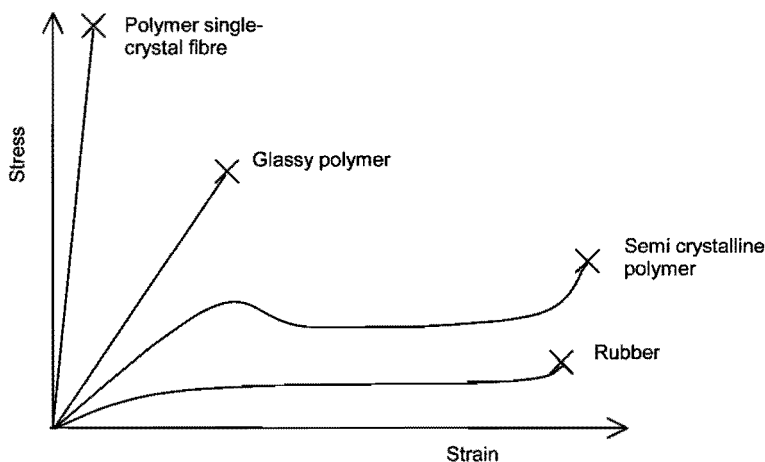


Figure 7.2. Mechanical properties for different types of polymers.

As a general overview, we can use Table 7.1 in which the different types of mechanical behaviour are related to the crosslink density.

Table 7.1. Possible mechanical behaviour for polymers.

	Glass/ceramic	Visco-elastic	Rubber elasticity
Thermoplast	$T < T_g$ High crystallinity	$T > T_g$ Low crystallinity	–
Elastomer	$T < T_g$	–	$T > T_g$
Thermoharder	Always	–	–

Intermezzo

The viscosity of polymers is obvious at low molar masses: they appear as molasses. At higher molar masses, the viscosity becomes so high that the polymer appears as a solid. However, upon increasing the temperature, the viscosity will decrease again, following the so-called WLF-equation:

$$\log(\eta) = \log(\eta_0) - \frac{17.4(T - T_g)}{51.6 + (T - T_g)}$$

Here, η_0 is 10^{12} Pa·s, and T_g is the glass transition temperature of the material.

7.2 Stiffness

The Young's modulus will be dependent on the temperature for most polymers, due to the glass transition. Of course, the amounts of crystallinity and crosslinking are also important, as can be seen in Figure 7.3.

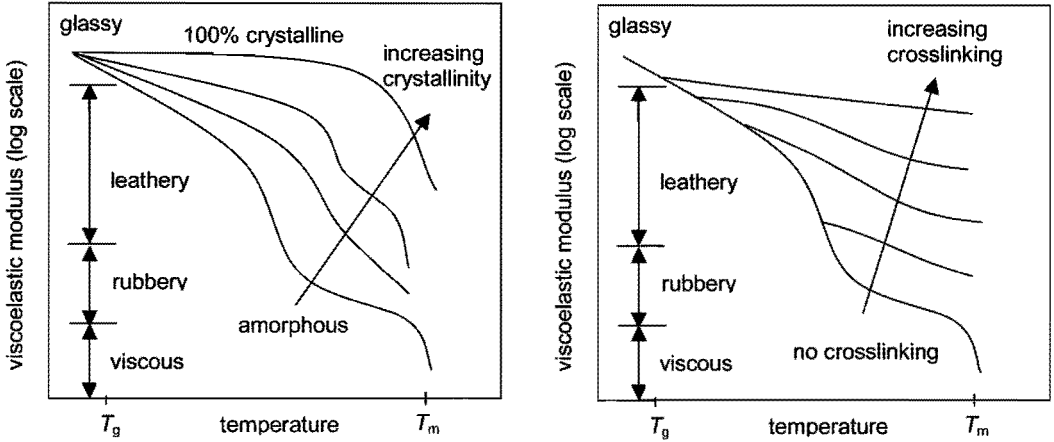


Figure 7.3. Young's modulus vs. crystallinity (left) and crosslinking (right).

Below T_g a polymer is glassy, and the Young's modulus depends on the strength of the bonds between the chains, as shown in Figure 7.4.

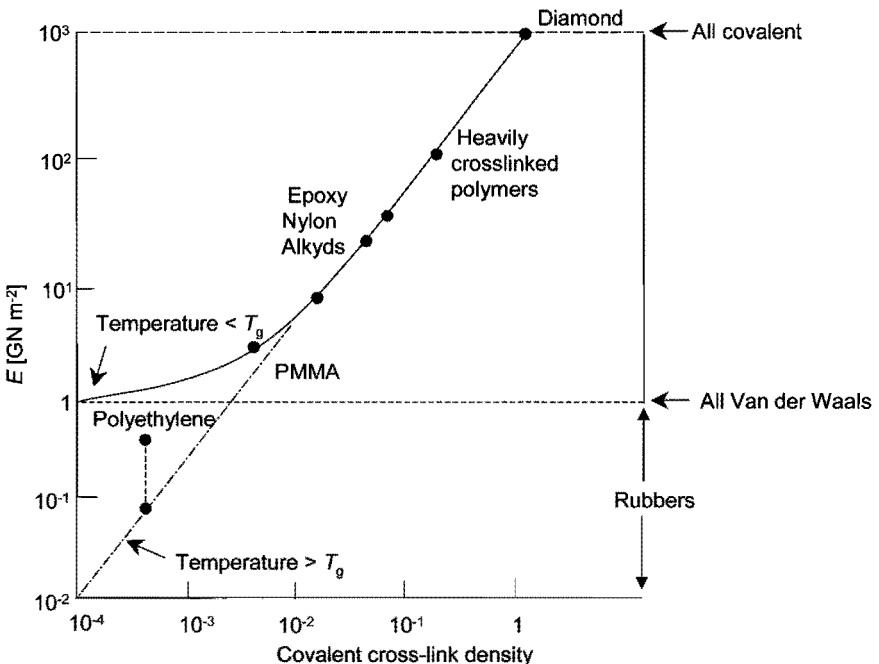


Figure 7.4. The crosslinks and the temperature determine the modulus.

7.2.1 Polymer crystals

Polymer crystals should behave as expected for inorganic crystalline materials, but this is not true: there is a very strong anisotropy in the Young's modulus. In the plane of the lamellae (see Figure 7.5) there are moduli of ca. 1 GPa (weak interactions between the chains), while perpendicular to the lamellae the moduli are ca. 100 GPa (the chains must be stretched).

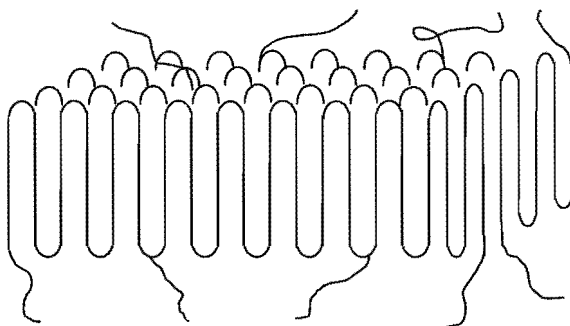


Figure 7.5. Lamellar structure of a polymer crystal.

The latter modulus can be predicted from the forces that are necessary to change bond angles and bond lengths in polymer chains.

In contrast to inorganic materials, polymers can never reach theoretical stiffness values (although we can come quite near), since it is nearly impossible to get 100% crystalline materials without defects.

Examples:

- Poly(propene) theoretically has a modulus $E = 50$ GPa, but in bulk PP one finds only $E = 2$ GPa, and for PP fibres $E = 20$ GPa.
- A specific nylon (PA66) even has $E = 160$ GPa in theory, but in the bulk only $E = 3.2$ GPa is found, and in fibres $E = 5$ GPa.

7.2.2 Semi-crystalline polymers

When there are both crystalline and amorphous parts in a polymeric material, the amorphous part gives flexibility, while the crystalline part gives the material strength. For crystallinities up to ca. 20%, there are small crystals in an amorphous matrix, and these polymers behave like crosslinked rubbers. When the crystallinity rises over 40%, the crystals start touching each other, and the material becomes stiff, and less visco-elastic.

In polymer crystals, the lamellae must unfold upon deformation (see Figure 7.6). This absorbs a lot of energy, and therefore semi-crystalline polymers have a high toughness (high W_f), but are not very stiff ($E \approx 2$ GPa). First, the amorphous between the lamellae is stretched, and then the lamellae themselves are reoriented. Then, the crystalline blocks are torn apart, and the segments are oriented with the amorphous chains in the draw direction.

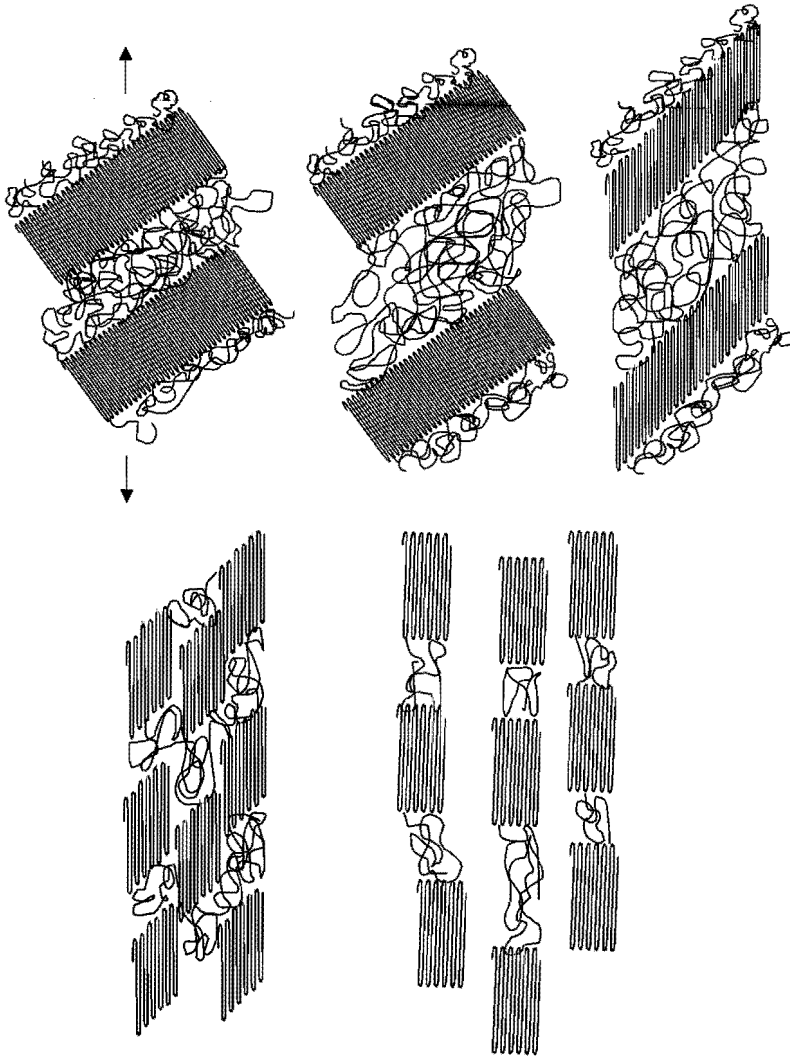


Figure 7.6. The various stages of deformation for a semi-crystalline polymer: stretching of amorphous part, deformation of crystals, and breakup of crystals.

7.2.3 Glassy state

The Young's modulus of the glassy state (amorphous, below T_g) is determined by both the primary, covalent interactions in the chain and the secondary, intermolecular forces between the chains:

$$\frac{1}{E} = \frac{f}{E_p} + \frac{1-f}{E_s}$$

Dependent on the contribution of E_p (value of f) the modulus can be as high as 100 GPa for oriented nylon fibres. This is comparable to e.g. copper.

7.3 Visco-elastic behaviour

In order to describe the visco-elastic behaviour of polymers in a mathematical way, one usually takes a mechanical model. However, we can also understand it at the molecular level: the long macromolecules can move along each other due to the weak interactions between them, and in this way the material can easily be deformed in addition to the stretching of bonds.

7.3.1 Models

An elastic solid behaves according to Hooke's law, where the Young's modulus E is important:

$$\sigma = E\varepsilon$$

This can also be written as:

$$\frac{d\sigma}{dt} = E \frac{d\varepsilon}{dt}$$

An ideal (Newtonian) liquid follows a different law, where the viscosity η determines which flow speed is caused by a certain stress (or pressure):

$$\sigma = \eta \frac{d\varepsilon}{dt}$$

A visco-elastic material has a mixture of these two properties, so it will show viscous flow due to stress, beside the elastic deformation. This can be seen in two phenomena:

- (i) a constant stress will lead to permanent elongation (**creep**);
- (ii) in a polymer that is kept at a constant elongation the stress will diminish (**stress relaxation**).

In Figure 7.7, we can see what the response is to a certain action. On the left we see creep due to constant stress, and on the right a constant strain leads to stress relaxation.

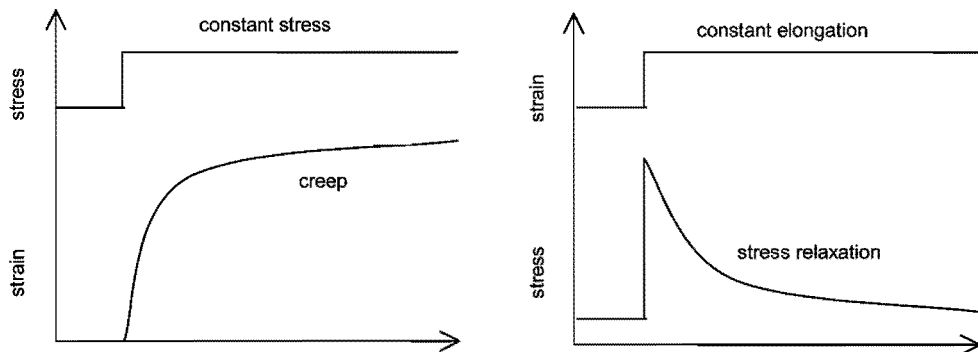


Figure 7.7. Creep (left) and stress relaxation (right) are typical for visco-elastic materials.

In order to describe these two types of behaviour, there are several models that use a mechanical analogue: a spring for the elastic part, and a piston for the viscous part. We will look at the models of Maxwell, Voigt (or Voigt–Kelvin), and linear elastic solid (or Zener) model (see Figure 7.8).

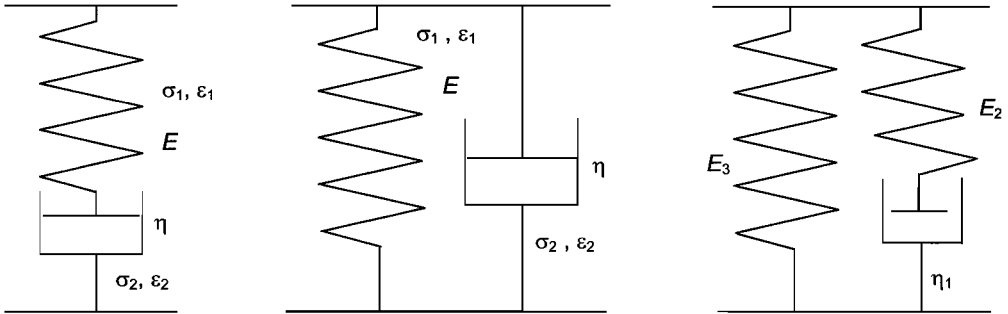


Figure 7.8. The three models used for visco-elastic behaviour: Maxwell, Voigt, and linear elastic solid.

7.3.2 Maxwell model

This simple model can (partly) describe stress relaxation: a spring ($\sigma_1 = E\varepsilon_1$) and a piston ($\sigma_2 = \eta d\varepsilon_2/dt$) are used in series, so the stress is the same:

$$\sigma_1 = \sigma_2$$

The strains, however, must be added:

$$\varepsilon = \varepsilon_1 + \varepsilon_2$$

So for the strain rate we can write:

$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_1}{dt} + \frac{d\varepsilon_2}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

Stress relaxation occurs when ε is constant (ε_c), so $d\varepsilon/dt = 0$:

$$\frac{d\sigma}{dt} = -\frac{E}{\eta} \sigma$$

With $\tau_r = \eta/E$, the relaxation time, and starting from $t = 0$, this integrates to:

$$\sigma = E\varepsilon_c e^{-t/\tau_r}$$

Here we see that the stress indeed decreases in time (see Figure 7.9). However, in real polymers the stress will never become completely zero as this model predicts.

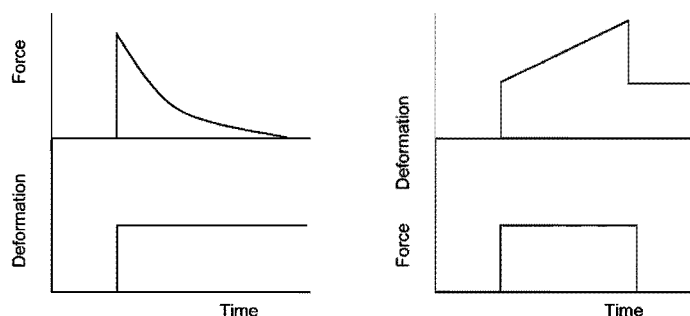


Figure 7.9. Stress relaxation (left) and creep (right) in the Maxwell model.

Creep is not predicted in a correct way at all by this model. Then we should have a constant σ (σ_c), and so $d\sigma/dt = 0$:

$$\frac{d\varepsilon}{dt} = \frac{\sigma_c}{\eta}$$

Starting from $t = 0$, this integrates to:

$$\varepsilon = \frac{\sigma_c}{E} + \frac{\sigma_c}{\eta} t$$

This is pure Newtonian flow, as for a liquid: the strain rate is constant, and does not level off (see Figure 7.9). A real polymer will have a maximum deformation for a certain stress.

7.3.3 Voigt model

This model can (partly) describe creep. Here, the spring ($\sigma_1 = E\varepsilon_1$) and the piston ($\sigma_2 = \eta d\varepsilon_2/dt$) are used in parallel, so the strains are the same:

$$\varepsilon = \varepsilon_1 = \varepsilon_2$$

Now, the stresses must be added, since both elements contribute:

$$\sigma = \sigma_1 + \sigma_2$$

This gives for the strain rate (with the same relaxation time $\tau_r = \eta/E$):

$$\frac{d\varepsilon}{dt} = \frac{\sigma}{\eta} - \frac{\varepsilon}{\tau_r}$$

By integrating from $t = 0$, creep can now be described for a constant stress σ_c :

$$\varepsilon = \frac{\sigma_c}{E} \left(1 - e^{-t/\tau_r} \right)$$

This is in good agreement with reality: creep is a non-linear process that reaches a maximum (σ_c/E), as shown in Figure 7.10. The deformation is completely reversible: when the stress is removed, the strain goes back to zero. However, there is no elastic behaviour at all.

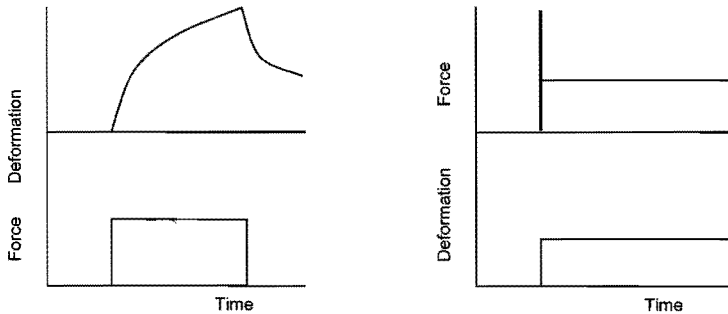


Figure 7.10. Creep (left) and stress relaxation (right) in the Voigt model.

Stress relaxation is described incorrectly. When ε is constant (ε_c), and $d\varepsilon/dt = 0$, it follows by integrating from $t = 0$:

$$\sigma = E\varepsilon_c$$

This is purely elastic behaviour: σ is constant (see Figure 7.10).

7.3.4 Linear elastic solid

Both previous models each describe a part of the visco-elastic behaviour, but another part incorrectly. We can combine them in the linear elastic solid model. Here, we have a Maxwell-element (spring 1 + piston 2 in series) in parallel with a second spring (3). For such an assembly the following relations hold:

$$\varepsilon = \varepsilon_1 + \varepsilon_2 = \varepsilon_3 \quad \sigma = \sigma_1 + \sigma_3$$

$$\sigma_1 = \eta_1 \frac{d\varepsilon_1}{dt} = \sigma_2 = E_2 \varepsilon_2$$

$$\sigma_3 = E_3 \varepsilon_3$$

After a lot of mathematical crunching, we get two relaxation times:

$$\tau_R = \frac{\eta_1}{E_2} \quad \tau_K = \frac{\eta_1}{E_3} \left(1 + \frac{E_3}{E_2} \right)$$

N.B.: These were called τ_ε and τ_σ , respectively, in the first edition of this book.

It then follows that:

$$\sigma + \tau_R \frac{d\sigma}{dt} = E_3 \left(\varepsilon + \tau_K \frac{d\varepsilon}{dt} \right)$$

For creep (σ constant at value σ_c from $t = 0$) this model then gives:

$$\varepsilon = \frac{\sigma_c}{E_3} \left\{ 1 - \left(1 - \frac{\tau_R}{\tau_K} \right) e^{-t/\tau_K} \right\}$$

There is a non-linear change of the strain in time to a maximum value (σ_c/E_3), and there is also an elastic part of the deformation ($\tau_R\sigma_c/\tau_K E_3$), which responds instantly ($t = 0$), as shown in Figure 7.11.

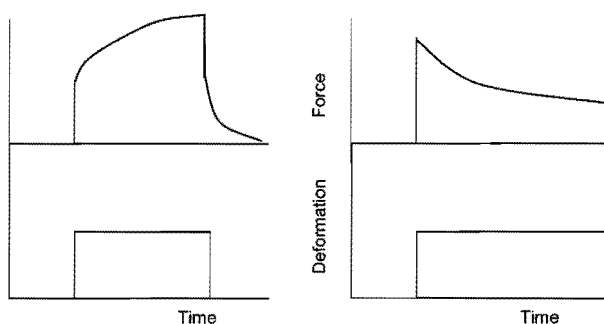


Figure 7.11. Creep (left) and stress relaxation (right) in the linear-elastic-solid model.

For stress relaxation (constant $\varepsilon = \varepsilon_c$ from $t = 0$) we can write:

$$\sigma = E_3 \varepsilon_c \left\{ 1 - \left(1 - \frac{\tau_K}{\tau_R} \right) e^{-t/\tau_R} \right\}$$

There is now a relaxation to a non-zero value ($E_3\varepsilon_c$), as seen in Figure 7.11.

So, this model can adequately describe both creep and stress relaxation. Remember, however, that it is just a mechanical analogue: we did not put the molecular structure into the description anywhere.

7.3.5 Dynamic mechanical measurements

In more realistic tests, the polymer is deformed in a dynamic fashion: it is stretched and relaxed periodically, either by tension or by rotation. This is the case for e.g. joints during walking, heart valves, and veins. In these cases, we can say that the deformation follows a periodic sine function:

$$\varepsilon = \varepsilon_{\max} \sin(\omega t)$$

Here, we use the angular frequency ω (rad/s), which is related to the normal frequency (ν [Hz]) by $\omega = 2\pi\nu$. The stress in the material will usually follow the strain (elastic behaviour), but there will be a time lag due to the viscous flow that also occurs:

$$\sigma = \sigma_{\max} \sin(\omega t + \delta)$$

The angle δ is the so-called **phase angle**, which indicates how much difficulties the stress has to follow the applied strain (see Figure 7.12).

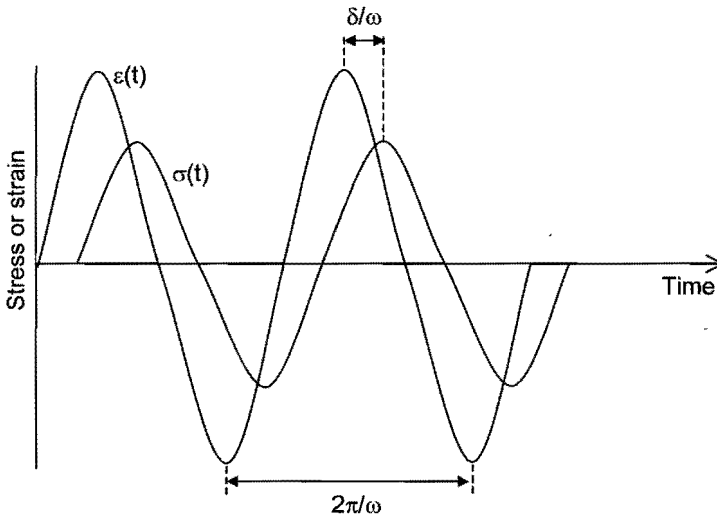


Figure 7.12. In a dynamic test of a visco-elastic material, stress and strain do not always follow each other directly.

For an ideal elastic material we see that $\delta = 0$, since the stress directly follows the strain. In a visco-elastic material the stress cannot follow the strain and δ is not zero. If we define $E = \sigma_{\max}/\varepsilon_{\max}$, we can write for the stress:

$$\sigma = \varepsilon_{\max} E \sin(\omega t + \delta)$$

According to the usual goniometric rules one can write:

$$\sigma = \varepsilon_{\max} E \cos(\delta) \sin(\omega t) + \varepsilon_{\max} E \sin(\delta) \cos(\omega t) = \varepsilon_{\max} \{E' \sin(\omega t) + E'' \cos(\omega t)\}$$

Here, δ is defined via the relation:

$$\tan(\delta) = \frac{E''}{E'}$$

and we have defined:

$$E' = E \cos(\delta) \text{ and } E'' = E \sin(\delta)$$

Some people prefer to write these two components of E as a complex number: $E^* = E' + iE''$. It can then be treated as a single quantity. There is then also a magnitude of this complex number: $|E| = (E'^2 + E''^2)^{1/2}$.

For a perfectly elastic material the stress is the same sine function as the strain (in-phase behaviour), so $\delta = 0$, $E' = E$ and $E'' = 0$. Because of this, E' is called the **elastic** or **storage component** of the modulus (reversible storage of elastic energy). For a liquid we have seen that $\sigma = \eta d\varepsilon/dt$, so when ε is a sine function, σ will follow a cosine function (out-of-phase behaviour): $\delta = 90^\circ$, $E' = 0$, and $E'' = E$. Therefore E'' is called the **loss** term: irreversible loss of energy due to viscous flow. You can actually calculate this energy loss during one cycle of the sine wave as the area under the σ, ε -curve:

$$W = \int_0^{2\pi/\omega} \sigma d\varepsilon = \pi \varepsilon_{\max}^2 E'' \text{ [J/m}^3\text{]}$$

The term $\tan(\delta)$ can be seen as a measure for the **internal friction** due to flow, which leads to hysteresis in the σ, ε -curve during stretching and relaxation.

7.3.6 Effect of frequency and temperature

At very low frequencies, the polymer behaves like an elastic rubber: E' is small, and so are E'' and $\tan(\delta)$. The material is easy to deform, and there is little loss.

At very high frequencies, the polymer can no longer follow the deformation, and behaves like an elastic glass: E' is large, and E'' and $\tan(\delta)$ are small. The material is hard to deform, but there is little loss.

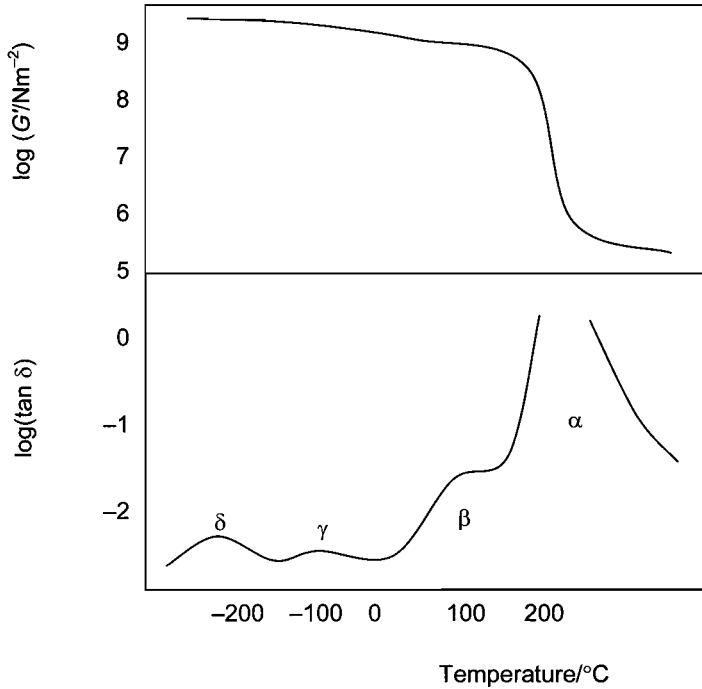
In an intermediate range of frequencies, the polymer is visco-elastic: E'' is large, and so is $\tan(\delta)$. The material has much energy loss due to internal friction.

This behaviour is a lot like the changes due to temperature: high frequency is similar to low temperature (glass), and low frequency is like high temperature (rubber).

The preceding story can also be told with the shear stress and strain, which usually can be measured more easily (torsional movements). In that case, we can just replace E' and E'' by G' and G'' .

During a variation of the temperature in a dynamic test, one can clearly see changes in the material due to e.g. the glass transition: they give a peak in $\tan(\delta)$. This is why a technique like DMTA (dynamic mechanical thermal analysis) is used a lot.

Example: The storage shear modulus and $\tan(\delta)$ for atactic (amorphous) poly(styrene) as function of temperature. α is the glass transition (movement of the main chain begins), and β , γ and δ are other transitions that are due to movements of other part of the macromolecule.



Can the models introduced above also predict this dynamic behaviour?
The Maxwell model gives with $\varepsilon = \varepsilon_{\max} \sin(\omega t)$:

$$E' = E \frac{\eta^2 \omega^2}{E^2 + \eta^2 \omega^2} \quad E'' = E^2 \frac{\eta \omega}{E^2 + \eta^2 \omega^2} \quad \tan(\delta) = \frac{E}{\eta \omega} = \frac{1}{\omega \tau_r}$$

This is a continuous decrease of the friction with frequency, which is not found in reality.

The Voigt–Kelvin-model gives the opposite behaviour:

$$E' = E \quad E'' = \eta \omega \quad \tan(\delta) = \frac{\eta \omega}{E} = \omega \tau_r$$

Here, we find a continuous increase of friction with frequency: also incorrect.

The more realistic linear elastic solid model gives:

$$E' = E \frac{1 + \tau_R \tau_K \omega^2}{1 + \tau_R^2 \omega^2} \quad E'' = E \frac{\omega(\tau_K - \tau_R)}{1 + \tau_R^2 \omega^2} \quad \tan(\delta) = \frac{\omega(\tau_K - \tau_R)}{1 + \tau_R \tau_K \omega^2}$$

Here, $\tan(\delta)$ has a maximum at an angular frequency:

$$\omega = \frac{1}{\sqrt{\tau_R \tau_K}}$$

(see Figure 7.13), and the modulus increases with frequency. This is a good description of real polymer behaviour.

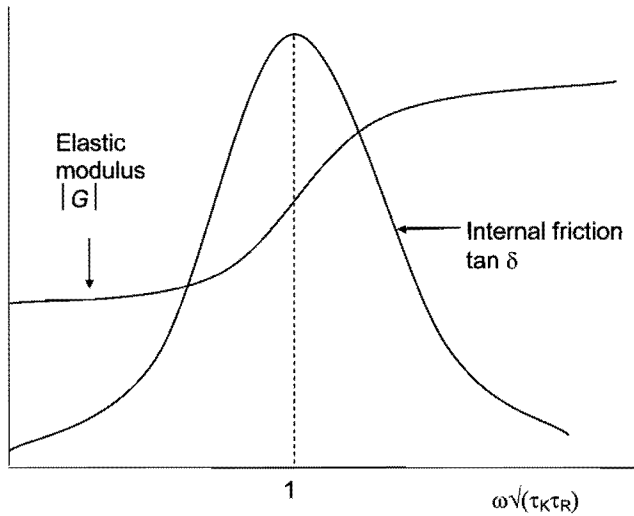


Figure 7.13. The linear elastic solid model gives a good description for the mechanical behaviour of a visco-elastic material.

For a biological material it is often seen that $\tan(\delta)$ has a flat maximum over a broad frequency range. This can be simulated by putting many linear elastic solid models in series, as shown in Figure 7.14.

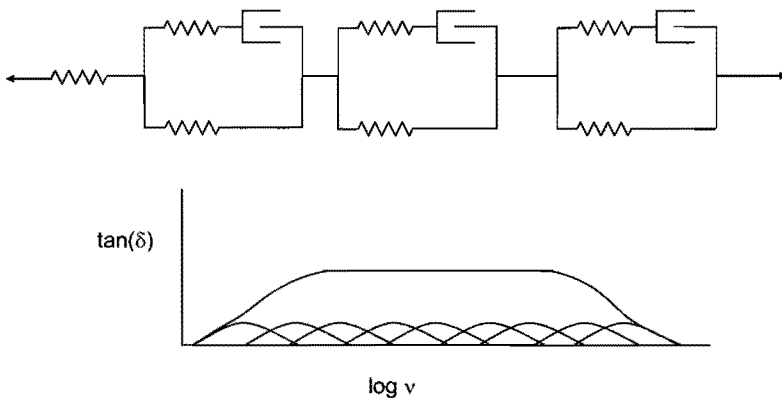


Figure 7.14. Model simulation for the behaviour of biological materials.

Intermezzo

There is a better model for the behaviour of polymers than with springs and pistons, but it is too complicated to treat here. The basic idea is that macromolecules move only along their length, as if they are restricted in a tube formed by the other macromolecules. This is why it is called the "reptation" model. By describing the macromolecule as strings of beads connected by springs, located on a three-dimensional lattice, this model gives an expression for the characteristic time (τ_d) a molecule needs to diffuse out of its tube. With these times, the response of molecules to a dynamic force can be calculated, and it turns out the prediction for G' and G'' as a function of frequency is quite good. However, because both the conformation and the movement of the macromolecules have to be described by statistical models, the mathematics are too complex to treat here.

7.4 Rubber elasticity

Rubbers are elastic materials, but they display a very strange (non-linear) relation between stress and strain. This is due to the fact that the elasticity is not due to the stretching of bonds (change in energy), but to changes in **entropy** during deformation. A random coil is the most probable situation (high entropy), while a completely stretched chain is very improbable (low entropy). Since entropy tends to a maximum, a force is needed to stretch a chain, even when there are no interactions keeping the chain together. Therefore, rubbers are often referred to as entropic springs.

In Appendix H it is derived (with the assumption $\Delta V = 0$) that the entropy change upon an elongation (or compression) λ follows the relation:

$$\Delta S \propto 3 - \frac{2}{\lambda} - \lambda^2$$

0.4 < λ < 1.3

From this it follows that $\Delta S < 0$ for both stretching ($\lambda > 1$) and compression ($\lambda < 1$). Also in Appendix H, the following relation between stress and elongation is derived for a rubber with a shear modulus G :

$$\sigma = G \left(\lambda - \frac{1}{\lambda^2} \right)$$

This equation indeed describes the behaviour of rubbers quite nicely for λ between 0.4 and 1.3 (see Figure 7.15).

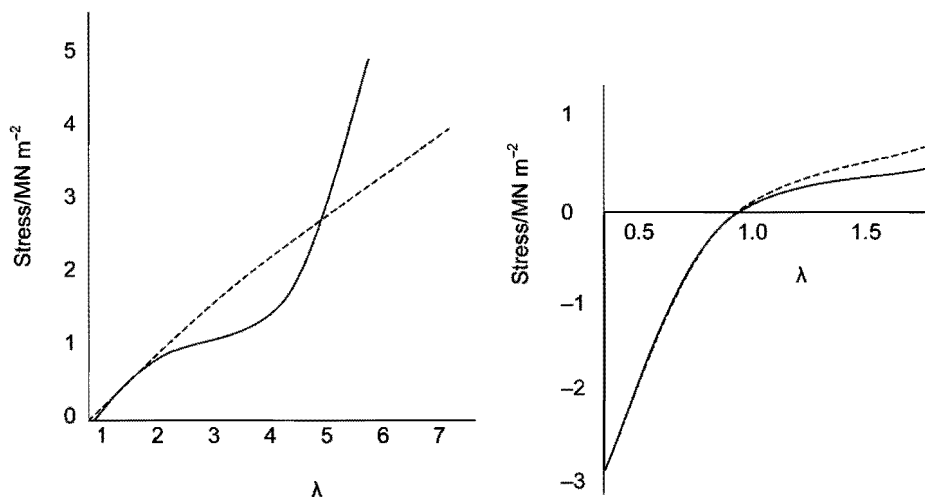


Figure 7.15. Experimental and theoretical (dashed line) behaviour of rubbers during tension and compression.

The value of G can be related to the distance between the few covalent crosslinks in the rubber network, and therefore gives an idea of the possible holes in the network (indicated by the so-called mesh-size), in which small molecules can be taken up. When the crosslink density increases, G becomes larger.

Also, we can write for the elongation factor λ :

$$\lambda = \frac{L}{L_0} = 1 + \varepsilon$$

For small values of ε ($\varepsilon \ll 1$) we can then approximately write:

$$\frac{1}{\lambda^2} = 1 - 2\varepsilon$$

Then the relation between σ and ε becomes:

$$\sigma = G(1 + \varepsilon - 1 + 2\varepsilon) = 3G\varepsilon$$

So: $G = \frac{E}{3}$. This is exactly what is expected for a rubber with a Poisson ratio (ν) of 0.5 (and indeed: in Appendix H, constant volume was assumed).

Intermezzo

In addition to the unexpected mechanical behaviour, there are two *thermomechanical* effects for rubbers that are also due to the importance of entropy changes.

1. The force F in these materials is almost completely determined by the entropy (see Appendix H), so when the temperature changes:

$$\frac{\partial F}{\partial T} = -\frac{\partial S}{\partial L} > 0$$

This means that when the strain is constant, the force increases when the temperature rises: rubbers want to shrink at higher temperatures, in contrast to normal materials.

2. It can also be derived what happens with the temperature when you stretch a rubber very quickly (so no heat can be exchanged with the surroundings):

$$\frac{\partial T}{\partial L} = -\frac{\partial S}{\partial L} / \frac{\partial S}{\partial T} = \frac{\partial F}{\partial T} / \frac{C_L}{T} > 0$$

So, rubbers will become warmer when you stretch them quickly.

7.5 Fracture

For fracture of crystalline or glassy polymers, Griffith's crack theory can be used as for inorganic materials. However, since the polymer chains can usually move past each other quite easily, we get the same effect as dislocation movement in metals: there is yield, and the work of fracture ($200\text{--}2000\text{ J/m}^2$) is much higher than the surface energy ($1\text{--}10\text{ J/m}^2$), so polymers are much tougher than ceramics.

The fracture stress is dependent on the molar mass of the polymer, since for longer chains there are more entanglements between the chains that prevent easy fracture growth:

$$\sigma_T = \sigma_{T,\infty} - \frac{C_f}{M_n}$$

We see that the tensile stress reaches a maximum value for infinitely high molar mass ($\sigma_{T,\infty}$). This is the same kind of behaviour we saw for the glass transition temperature in Chapter 6.

Intermezzo

Besides yield with necking, there can also be plastic deformation in polymeric materials by *crazing*: some of the chains are stretched, and this region appears quite different under the microscope. Crazes look like cracks, but they are not.

7.6 Mechanical properties of biopolymers

The mechanical properties of biopolymers are often strongly dependent on the surrounding medium: especially the water content is very important. Water acts as a **plasticizer**: it increases the mobility of the polymer chains. A common problem with studying these materials is that *in vivo* and *in vitro* results are quite different: the remark “dead and fresh” is often seen. Keeping a biopolymer out of the body for a longer time, treating it against decay, or even drying it can drastically change the properties.

A general property of biopolymers is the surprisingly high fracture strength and toughness. This can be explained by the fact that most biopolymer materials consist of smaller modules, which are hierarchically built up to larger structures. Since the modules can be stretched by unfolding them one by one, the material as a whole can absorb a lot of energy before it is stretched to breaking (see Figure 7.16).

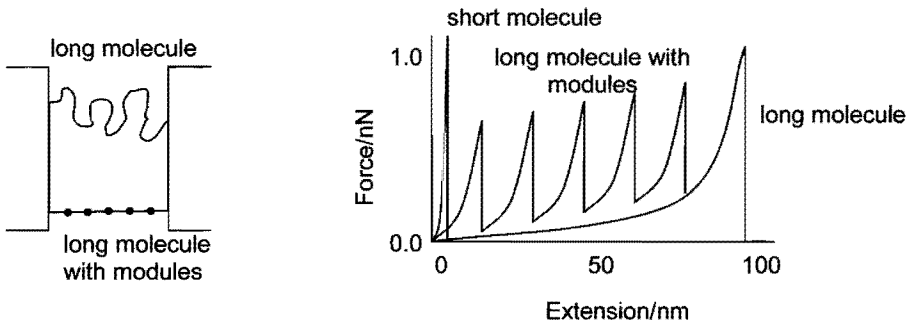


Figure 7.16. Mechanical behaviour for short, long, and modular materials.

7.6.1 Proteins

Collagen: in dry form it is rather stiff and brittle ($E = 6$ GPa). When wet it is softer: first the modulus E is very low, because the folded structures in the fascicles are unfolding (the “toe” in Figure 7.17), and above a certain strain a modulus of $E = 1\text{--}1.5$ GPa is found (the “heel”). The maximum elastic strain is 1–2%. Collagen *in vivo* is often continuously under stress by movement (e.g. tendons) or prestressing (e.g. in walls of blood vessels). At a maximum strain of 10% collagen breaks (fracture stress: 10–100 MPa).

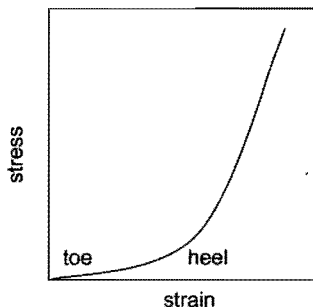


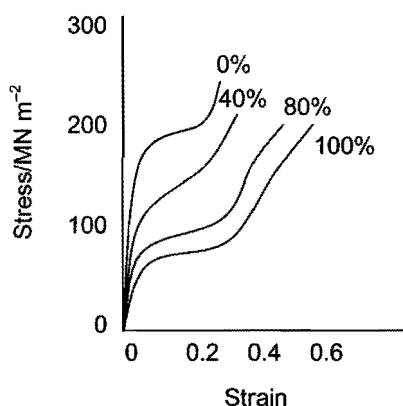
Figure 7.17. General mechanical behaviour of collagen.

Keratin: Most materials with keratins are actually composites, since there is an amorphous matrix around fibres. Up to a strain of 2% keratin is elastic with $E = 4$ GPa. After that it shows yield: the modulus E becomes much lower, since the α -helices unfold to β -sheets. At a strain of 30%, E increases again, because all helices are completely unfolded.

Also here, water functions as plasticizer: a higher water content gives yield at lower stresses and higher strains. The modulus of the matrix can decrease from 6 GPa to 1 GPa. In addition, these materials become anisotropic at high water content, since the fibres start orienting in a parallel fashion in the ever softer matrix.

Keratin materials show a large hysteresis, and are therefore hard to break: the work of fracture is 10 kJ/m^2 , which is typical for modern high-performance composites. We will look at the behaviour as composite material later in Chapter 9.

Example: Wool (sheep hair) shows a strongly different behaviour when the humidity in the air changes from 0% to 100%. This is the same reason why hairdressers wet hair before cutting it.



Silk: This is a semi-crystalline polymer, in which the fibres are strongly oriented due to the natural spinning process. The crystalline areas give strength, while the amorphous matrix ensures elasticity. Again, the presence of water is very important.

Along the fibres silk is very stiff ($E = 10$ GPa), but due to the weak interactions between the layers it can stretch to strains of 25–28% until it breaks at 1–1.3 GPa. The work of fracture is $12\text{--}18 \text{ MJ/m}^3$. These properties are very similar to modern nylon fibres.

Elastin: This protein behaves like a typical rubber, with $G = 0.6$ MPa. Above a strain of 100% the stress increases strongly, since the crosslinks are now loaded (see Figure 7.18).

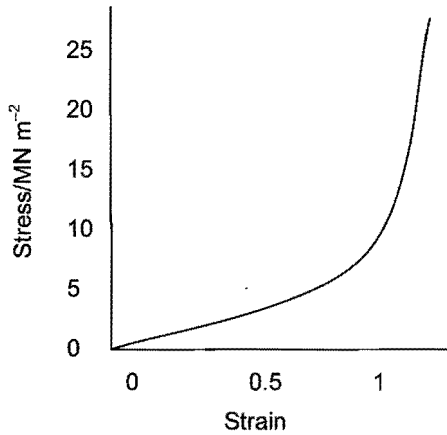


Figure 7.18. Mechanical behaviour of elastin.

A good model for elastin is the protein poly(GVGVP), which shows contraction upon raising the temperature, or upon the addition of salts or acids. These latter effects are due to the decrease of electrostatic repulsion, since COO^- is transformed to COOH (acid), or by decreasing the dielectric constant (salts).

7.6.2 Polysaccharides

Cellulose fibres: Because of the many hydrogen bonds, cellulose is very stiff ($E = 140$ GPa), but this decreases upon the addition of water. The angle with which the fibres are wound in the material is also very important: E can become 8 times smaller when the angle changes from 0° to 40° .

Gels: These are visco-elastic materials that are more on the viscous side. There are only a few stable crosslinks, so flow is very easy. Some plant gels (alginates) can be more elastic, since there are more crosslinks. Gels are usually parts of composite materials (see Chapter 9). Of the various type of GAG, hyaluronic acid is found most frequently, e.g. in the vitreous matter in the eye and in the synovial fluid.

Due to the large quantities of water in these polyelectrolytes, the volume of these gels is very high and there is a lot of overlap between the chains, giving weak crosslinks. At high shear rates, hyaluronic acid gels change from elastic to more viscous behaviour (shear thinning), which is used in joints to give good lubrication.

Problems

7.1. Give the expected mechanical behaviour of the materials given below. Indicate for each pair the most important difference between the materials.

- Isotactic linear PP ($M_w = 120$ kg/mol) vs. atactic linear PP ($M_w = 100$ kg/mol).
- Branched PVC, DP = 2000 vs. heavily crosslinked PVC, DP = 2000.
- Random copolymer of styrene and butadiene ($M_n = 100$ kg/mol, 10% of the sites crosslinked, 20 °C) vs. random copolymer of styrene and butadiene ($M_n = 120$ kg/mol, 15% crosslinked, -85 °C).
- Poly(isoprene) (100 kg/mol, 10% crosslinks) vs. poly(isoprene) (100 kg/mol, 20% crosslinks).

7.2. A piece of polymer is stressed to a level of 28 MPa and its length is held constant. After 30 days the stress has fallen to 17 MPa. How long will it take for the stress to fall to 7 MPa if this is a Maxwell solid?

7.3. Ten minutes after a stress of 7 MPa was applied to a polymer rod with an elastic modulus of 700 MPa, the strain was measured to be 0.005.

- What is the viscosity of this polymer if it behaves like a Voigt solid?
- After 1000 minutes, what strain can be expected?

7.4. A polymer that can be described as a linear elastic solid shows creep.

- If $\epsilon = 0.005$ at $t = 0$, and $\epsilon = 0.02$ after waiting very long, what is then the value of τ_R/τ_K for this polymer?
- Describe this creep, and the constant strain after a long time, in terms of macromolecules.
- This polymer shows maximum internal friction at $\omega = 10$ rad/s. Calculate τ_K and τ_R , and the value of $\tan(\delta)$ at $\omega = 5, 10$, and 15 rad/s.

7.5. An elastomeric material is stretched 20% under a tensile stress of 0.25 MPa. Calculate the stresses necessary for stretching this material 50%, and compressing it 20%.

7.6. A poly(styrene) component must not fail when a tensile stress of 1.25 MPa is applied. Determine the maximum allowable surface crack length if the surface energy of PS is 0.50 J/m². Assume a modulus of elasticity of 3.0 GPa (glassy state).

7.7. For a plate of a brittle polymer with thickness (t) 5 mm and width (b) 25 mm we find a tensile strength of 85 MPa, when there is a notch on the side of the plate. For this kind of situation it is known that the following formula holds for the fracture toughness:

$$K_{1C} = Fa^{1/2}/(b \times t) \times \{1.99 - 0.41(a/b) + 18.7(a/b)^2 - 38.48(a/b)^3 + 53.85(a/b)^4\}$$

Here, F is the force on the material, and a is the length of the crack in the material. If we know that $K_{1C} = 1.25$ MPa·m^{1/2}, calculate the length of the cracks in the material that was tested.

Hint: Can this horrendous formula perhaps be approximated by something simpler?

7.8. For PMMA it is found that the tensile strength depends on the molar mass: 107 MPa at 40 kg/mol, and 170 MPa at 60 kg/mol.

Predict the tensile strength at a molar mass of 30 kg/mol.

7.9.* For the visco-elastic behaviour of poly(styrene) it is known that: $E = 3 \text{ GPa}$, $\tau_K = 0.01 \text{ s}$ and $\tau_R = 0.005 \text{ s}$.

- a. Calculate the energy that this polymer takes up during a dynamic load of $\omega = 100 \text{ rad/s}$ with a maximum strain of 0.02.
- b. Explain this energy uptake in terms of macromolecules.
- c. Why could this energy uptake be relevant for a biomedical application of this polymer?

8 Changing material properties I: Microstructure

In order to change the material properties of existing materials, there are two quite different approaches:

(i) Try to change the structure of the material itself, by some processing technique, or by choosing the chemical composition in a particular way. These possibilities will be treated in this Chapter.

(ii) Try to combine different types of materials in a composite. This is often found in biological materials, and will be treated in the next Chapter.

The only activities worth doing in the long run are the searching of knowledge
and the creation of beauty.

Arthur C. Clarke
(1917–2008)

8.1 Changing metal properties

In metals, the mechanical properties (except elasticity!) are mainly determined by imperfections in the crystal structure. Specifically, the mobility of dislocations is important for the yield strength, and the growth of cracks determines the fracture strength. This last property is also dependent on the work of fracture, or the fracture toughness, which itself is strongly dependent on the mobility of dislocations.

If we want to change the mechanical properties of these materials, we must therefore change the mobility of the dislocations. When the mobility of the dislocations is decreased, the metal gets a higher yield strength and a higher tensile strength (for ductile fracture), but its toughness will go down: stronger but more brittle. When the mobility of the dislocations is increased, the yield stress will go down, but the toughness will increase: weaker but more ductile. Toughness and strength are therefore contradictory demands!

N.B.: For metals we often say strength when we are actually discussing the yield stress, since this indicates the start of plastic deformation, which is detrimental for its use as construction material. However, sometimes the fracture stress or ultimate tensile stress is meant. Be careful!

8.1.1 Strengthening

The mobility of dislocations can be *decreased* by creating more dislocations that interfere with each other, by creating higher tension in the crystal lattice, or by making more barriers for movement. Methods for this are:

- Materials in which several phases (regions with different chemical composition) are present. We can then speak of a specific microstructure, with many barriers. This will be treated in more detail in section 8.2.
- Inserting atoms with a different diameter in a lattice also creates more tension. These materials are often called **solid solutions** (see Figure 8.1).
- **Precipitation hardening** gives more tension by inserting small crystals of another material in the lattice (see Figure 8.1).

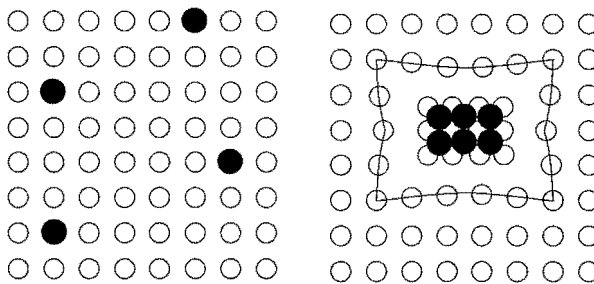
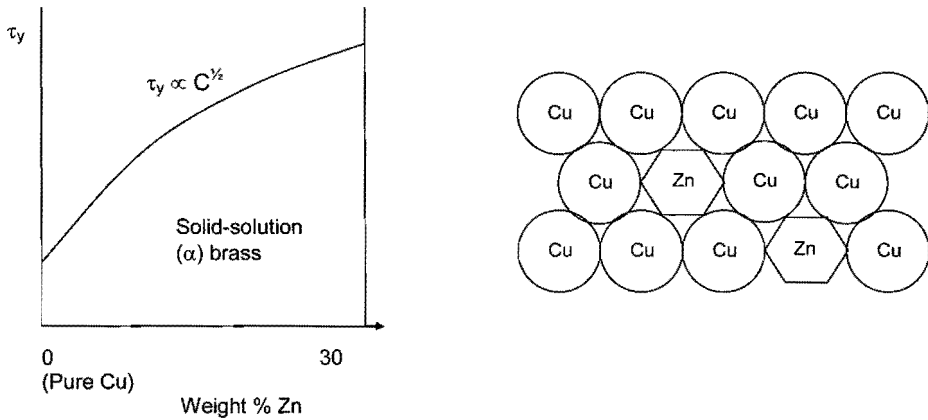


Figure 8.1. Solid solutions (left) and precipitates (right) lead to lower mobility for dislocations.

Example: Cu/Zn alloys (brass); yield strength increases when the Zn-content rises.



- **Dispersion hardening** is basically the same phenomenon as precipitation hardening, but with larger particles in the matrix. This will also give more grain boundaries, and therefore more barriers. Actually, we are now making a kind of composite of a metal and another material (see Chapter 9).

- **Cold working** (or cold rolling, see Figure 8.2) creates more tension in the lattice by plastic deformation, and also increases the number of dislocations. This is the same as the strain or work hardening we mentioned in section 2.2.

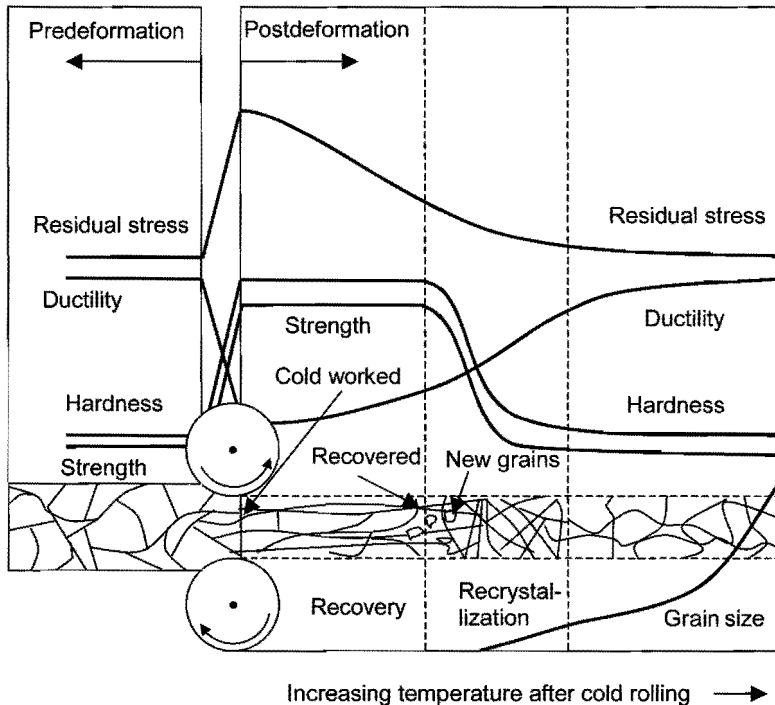


Figure 8.2. Cold working and annealing have a strong influence on dislocation mobility.

8.1.2 Toughening

The mobility of dislocations can be *increased* by removing tension in the crystal lattice, or by removing barriers for movement. Methods for this are:

- **Annealing** (or tempering, see Figure 8.2) and recrystallization: this will restore the effects of cold working, and will lead to fewer dislocations and less tension. The toughness then goes up (as seen in the ductility or the reduction in area), but the strength and hardness go down (see Figure 8.3).

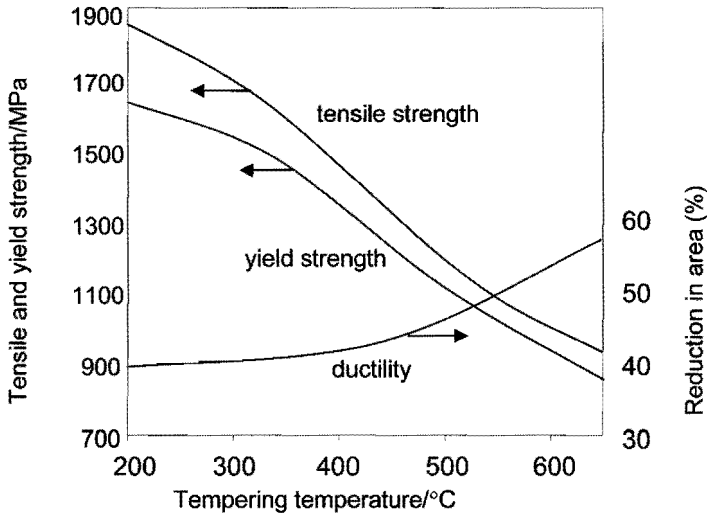


Figure 8.3. Effect of annealing on mechanical properties of metals.

- Less contaminations in the metal: there will be less tension in the lattice. So a pure metal is easier to deform.
- Materials with only one phase: fewer barriers due to phase boundaries. This will be discussed in the next section.
- Changing the lattice type: FCC instead of HCP/BCC gives an easier deformation (more slip systems). This again related to phase diagrams, and will be treated later.

Example: Iron can be forged better at higher temperature, since it then changes from α -Fe (BCC) to γ -Fe (FCC).

8.1.3 Grain size

The only parameter that can increase both the strength (yield stress) and the toughness is the grain size. This is true for both polycrystalline metals and polycrystalline ceramics.

The first effect has already been discussed: small grains have a lot of grain boundaries that restrict the mobility of dislocations, and therefore the yield stress is high. Thus, the material is stronger for smaller grains.

There is a general relation between the yield stress of a polycrystalline material (σ_Y) and the grain size (d_g), related to the yield strength of a single crystal ($\sigma_{Y,sc}$):

$$\sigma_Y = \sigma_{Y,sc} + \frac{C_g}{\sqrt{d_g}}$$

However, since smaller grains give more grain boundaries, and these are also weak places in the material, there are also implications for fracture. Cracks will preferentially grow along the grain boundaries. But for small grains, the grain boundaries form a very twisting path, and the cracks must change direction so often, that a lot of energy is lost before the crack is large enough to fracture the material. Therefore, there is a high work of fracture, and a high toughness.

Example: Flint is a form of microcrystalline quartz that is very hard. Transparent flint has a rupture strength of 190 MPa, and a grain size of less than 1 μm . Opaque flint has much larger grains (2–10 μm), and also a smaller strength: 120 MPa.

An optimal and uniform grain size distribution is very important for the mechanical properties of a polycrystalline material. Rapid cooling of a molten material often results in small grains. However, during cooling several other unexpected things can happen: for this, we have to take a look at phase diagrams in the next section.

8.2 Phase diagrams

In order to understand a bit more about the effect of different phases in a material, and the effect on the microstructure, we must be able to read and interpret **phase diagrams**.

The definition of a **phase** is: a region of the material with a different aggregation state (gas, liquid, solid) and/or a different chemical composition.

The most simple example of a phase diagram is the case of one compound (so the chemical composition is always the same) with different aggregation states.

Figure 8.4 shows the phase diagram of water, where we only see which phase (here: aggregation state) is present at a particular temperature and pressure.

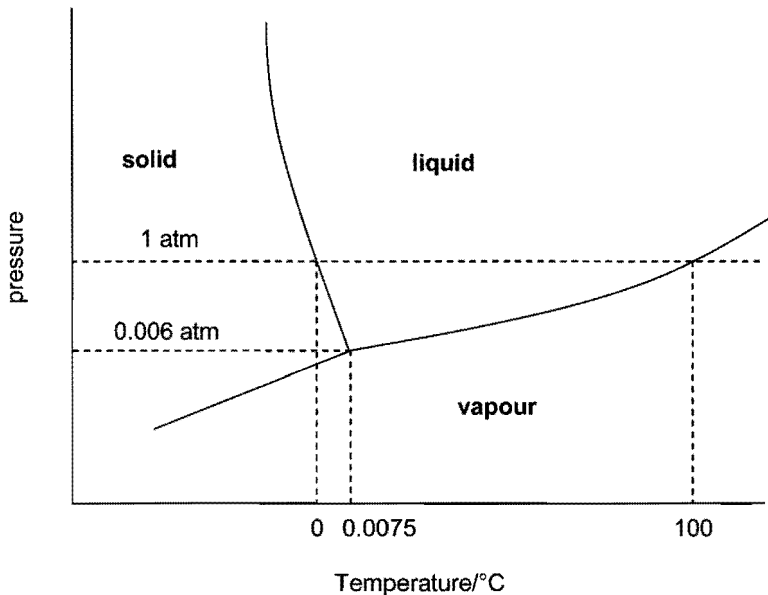


Figure 8.4. Phase diagram of water: depending on pressure and temperature, three phases can be present.

Much more important for materials science are the phase diagrams of at least two components: **binary phase diagrams**. Now the chemical composition of the phases can also change. Usually we choose a constant pressure (1 bar), and look only at the effects of temperature and composition. Let's take a look at the phase diagram of copper and nickel (figure 8.5). Chemical composition (always with symbol x) can be indicated in atomic percentages (mole fractions), but more commonly in weight (or mass) fractions. Here we will use wt% nickel.

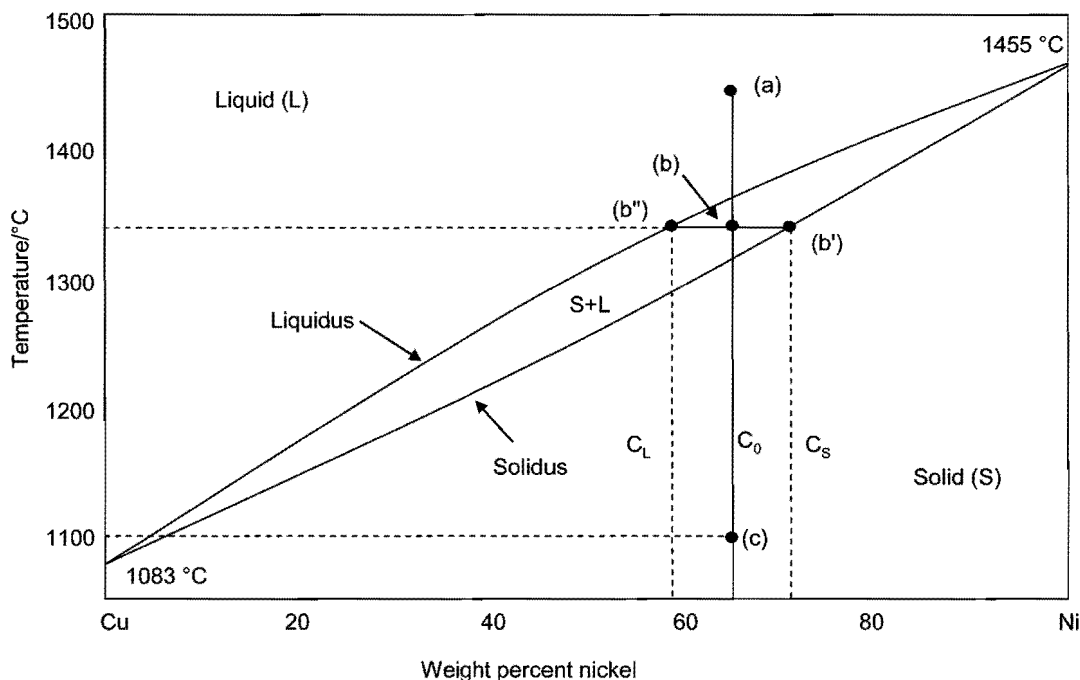


Figure 8.5. Binary phase diagram of copper and nickel at 1 bar.

What can we see in this binary phase diagram? At 0 wt% Ni (pure Cu) and 100 wt% Ni, we see the melting points of the pure compounds. When we take a melt with 65 wt% Ni (C_0) at 1450 °C (a), we have one phase: a liquid. Therefore, this region of the diagram is marked “L”. At low temperatures (c), we see only a solid (S), which is a mixture (an alloy) of copper and nickel. Of course, the chemical composition here is also 65 wt% Ni. However, during the cooling process, several strange things happen, and these can be read from the phase diagram.

When we cool the liquid starting from 1450 °C, we will see something happen for the first time at ca. 1360 °C, when we reach the area marked “S+L”. This area is a forbidden area for this mixture: it must separate into a liquid phase (on the **liquidus** line) and a solid phase (on the **solidus** line). What is very important is that the first solid material to come out of the liquid has a chemical composition of ca. 78 wt% Ni: it contains much more nickel than the liquid. This means that Ni tends to solidify before Cu, and that Cu will follow at lower temperatures.

At point (b) at ca. 1340 °C, this has changed: the solid (b') now has a composition of 72 wt% Ni (C_S), and the liquid (b'') has a composition of 60 wt% Ni (C_L). Since the liquid and the solid phase have the same temperature, we can connect them with a horizontal line: the **tie line**.

When we cool even further, we will continue to see a change in composition of the phases: the solid phase will follow the solidus line, and the liquid phase will follow the liquidus, both moving to the left.

At a temperature of ca. 1310 °C, we reach the area marked “S”: this means that we will see one phase only, which is a solid. The composition of this solid will be (of course) 65 wt% Ni. After that, the solid will simply cool to e.g. 1100 °C (c).

During this cooling, we will see not only changes in the *chemical* composition of the liquid and the solid, but their quantities must also change: we start with 100% L, and we must end up with 100% S. How can we see what happens in between? For this, we can use a simple construction with the horizontal line that connects the solid and the liquid: it is cut into two parts by the average composition, which must of course stay the same in the whole experiment. We use the tie line to determine the chemical compositions of the solid phase (x_1), the liquid phase (x_2), and we know the average composition of the system (x_0), which is also the starting composition. We can then use the so-called **lever rule** to calculate the mass fractions of solid (f_1) and liquid (f_2) (the *physical* composition of the system):

$$f_1 = \frac{x_2 - x_0}{x_2 - x_1} \quad f_2 = \frac{x_0 - x_1}{x_2 - x_1}$$

(If you want to be convinced why this rule works: see Appendix K.)

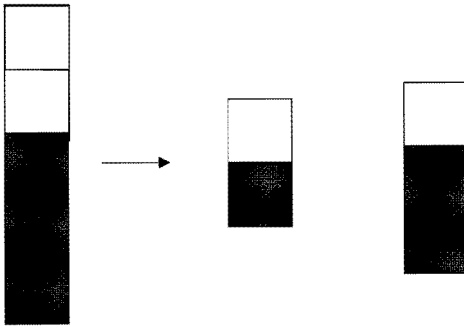
Be careful: these f_i are also fractions (weight or mole), but are e.g. wt% L, and never wt% Ni! They represent the way the whole system is split into different phases.

To help with all the symbols, perhaps this simple example is of use:

$$m_0 = 5 \\ x_0 = 3/5$$

$$m_1 = 2 \\ f_1 = 2/5 \\ x_1 = 1/2$$

$$m_2 = 3 \\ f_2 = 3/5 \\ x_2 = 2/3$$



So, we can calculate for every temperature during the cooling how much liquid and how much solid is present. And of course we can also see what the composition is of the phases that are formed at each temperature (where the tie line intersects the liquidus and the solidus). So, we can perform a complete physical (amount of liquid and solid) and chemical (composition of phases) analysis. Please take care: you must decide yourself which phases you call 1 and 2! It is not always so that 1 is solid and 2 is liquid. If you forget this, all your calculations will be the wrong way around.

In Figure 8.6 we see the cooling process for a copper–nickel mixture with 35 wt% Ni. The compositions of the formed phases are indicated. Use the lever rule to check whether the amounts of liquid and solid are correct. Note that the solid phase is now called α , something that happens a lot in phase diagrams. You can always use the name as indicated in the diagram.

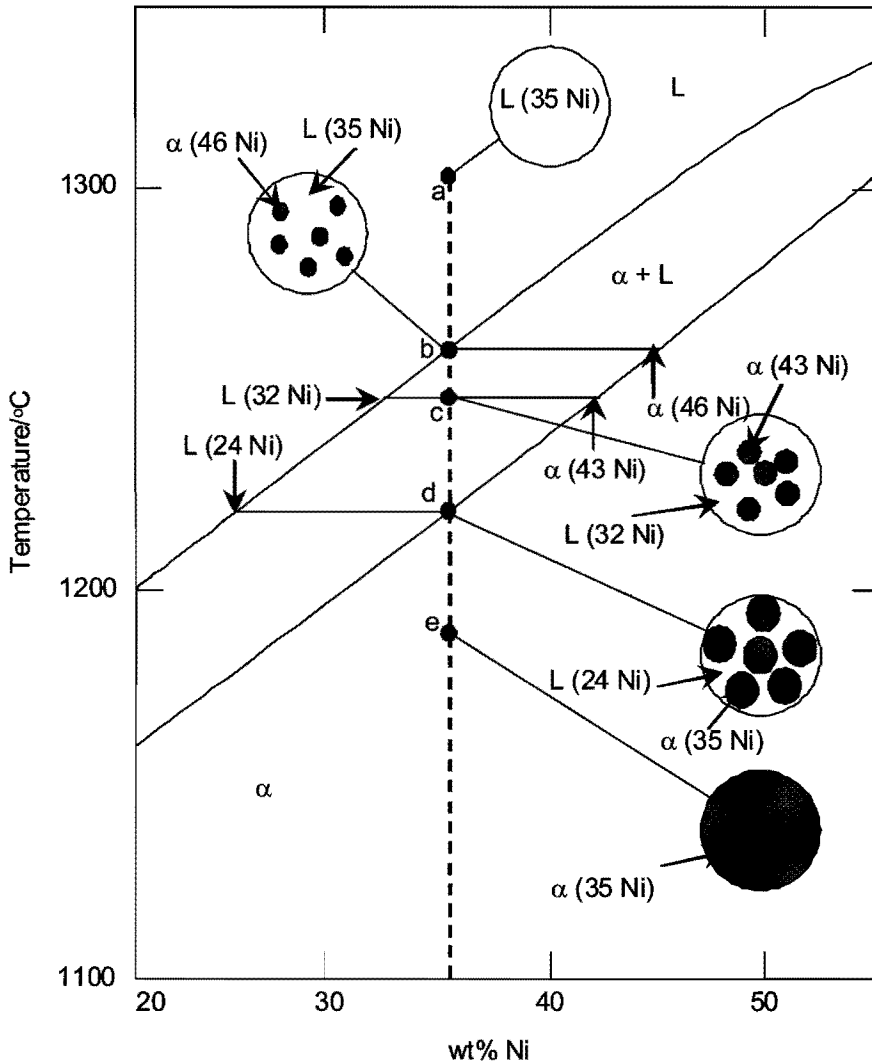


Figure 8.6. Cooling process for a 35 wt% Ni melt.

Intermezzo

Why is this important for the materials scientist? Since a solid material that is once formed will usually not change quickly in chemical composition, we can sometimes see the formation of various layers during cooling, each with different chemical composition. The first grains of solid will be 46 wt% Ni, and the last solid to form will be 35 wt% Ni. Since we saw earlier that the presence of strange atoms in a lattice will influence the mechanical properties, this microstructure will be very important. The phenomenon of getting different layers in the grains is called coring, and will happen e.g. at rapid cooling from the melt.

8.2.1 Phase rule

We can conclude something else about the cooling process, but for that the **phase rule** must be introduced. We will not show here why it is valid (see Appendix J), but we will simply apply it to our phase diagrams. The phase rule says that with a certain number of **components** (C), and a certain number of phases (P), we can only choose a restricted number of parameters, the **degrees of freedom** (\mathcal{F}):

$$\mathcal{F} = C + 2 - P$$

What does this mean? We will look only at binary phase diagrams: there will be two components ($C = 2$). The number of phases can be read from the phase diagram: $P = 1$ for the regions marked "L" and "S", and $P = 2$ for the region marked "S+L". We will later see that $P = 3$ is also possible.

The parameters that can be chosen freely are usually: temperature, pressure, and chemical composition. In our binary phase diagrams, we usually set the pressure at 1 bar, so that choice has been made: \mathcal{F} is 1 lower than allowed by the phase rule. That leaves us with:

$$\mathcal{F} = 3 - P$$

So, when $P = 1$ (e.g. for a liquid melt), we have $\mathcal{F} = 2$: we can choose the temperature and chemical composition of the melt freely, as long as we stay within the region marked "L". When we are in the region marked "S+L" (both a solid and a liquid phase), we have $P = 2$ and so $\mathcal{F} = 1$: we can set the temperature, but the chemical compositions of both phases are completely determined by the solidus and liquidus lines. They are no longer free.

When we now look at a phase diagram like that of lead and tin (solder), we see another phenomenon: the **eutectic** (see Figure 8.7).

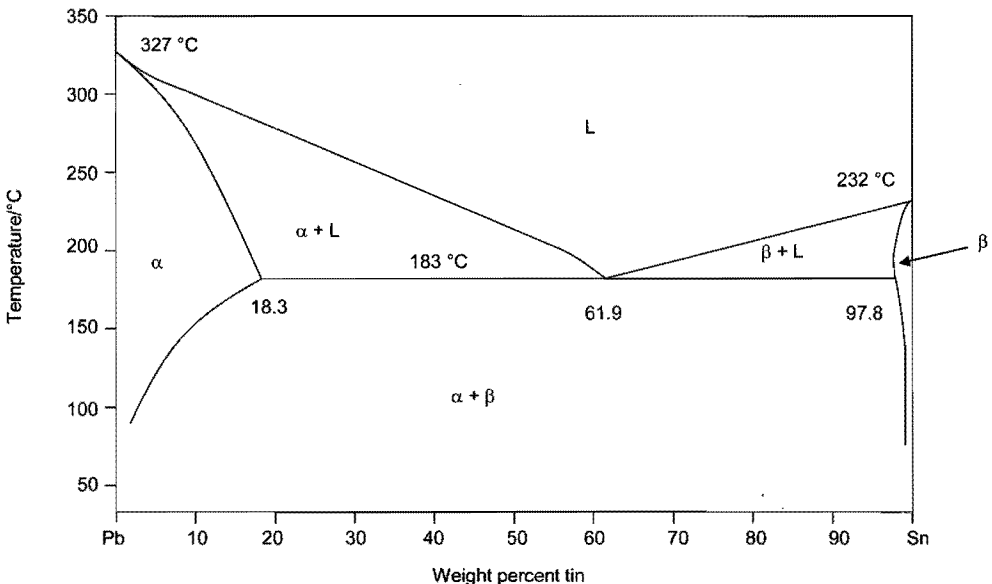


Figure 8.7. The phase diagram of lead and tin at 1 bar.

This means that there is a possibility of three phases coexisting in the material: here at 183 °C we see that there are a solid (α , 18.3% Sn), a liquid (L, 61.9% Sn), and another solid (β , 97.8% Sn) present at the same time. Now $P = 3$, so $\mathcal{F} = 0$: we can not choose anything freely. Both temperature and all chemical compositions are fixed by the diagram. This also means that the three-phase region is only a horizontal line, and not a two-dimensional region like the one-phase or two-phase areas. There can also be vertical lines in a diagram like this: compounds with a very narrow range for the chemical composition. These can also occur on the y-axes!

Intermezzo

When cooling water, we have $C = 1$ (H_2O), and when the pressure is chosen at 1 bar, we have: $\mathcal{F} = 2 - P$. For liquid water, we have $P = 1$, so $\mathcal{F} = 1$: we can freely choose the temperature (between 0 and 100 °C, of course). However, at 0 °C we also get ice (solid phase), and so $P = 2$, and $\mathcal{F} = 0$: we can withdraw heat, but the water and the ice will stay 0 °C until all liquid is gone, and we again have one phase (solid ice). Then we can lower the temperature again.

Let's start by cooling a melt with exactly the eutectic composition of 61.9 wt% Sn (see Figure 8.8). There will be liquid until we reach the eutectic temperature (183 °C). Then, both α and β are formed simultaneously as two new solid phases: we have 3 phases, so no degrees of freedom, and the temperature stays constant. When we keep on removing heat, the liquid will finally disappear, and only α and β will be left: we enter the " $\alpha + \beta$ " region, and the temperature can start decreasing again. From the lever rule we can calculate that just below the eutectic there will be 55 wt% β and 45 wt% α .

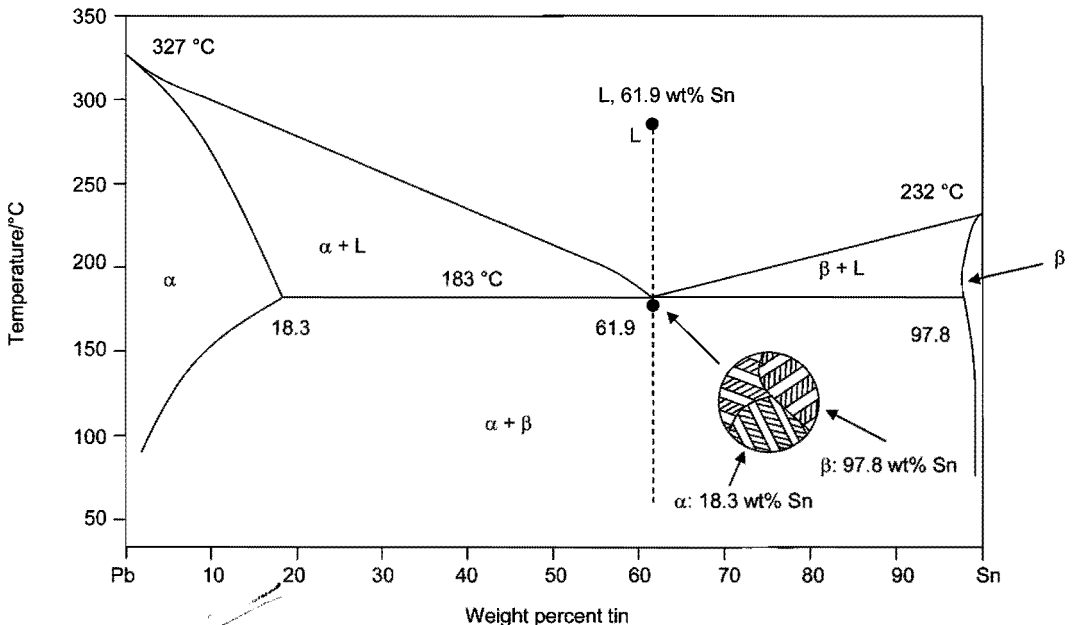


Figure 8.8. Cooling a melt at 61.9 wt% Sn (eutectic composition) gives a layered structure of α (white) and β (dashed).

The solid that is now formed has—of course—the eutectic composition, but it also shows a characteristic layered structure. How is this microstructure formed? The only way in which both α and β can be formed simultaneously as solids from a liquid melt is by growing “sideways” in parallel layers, as shown in Figure 8.9. The atoms in the melt will move by diffusion to the layers in which they prefer to crystallize in higher concentration (Pb to α , and Sn to β).

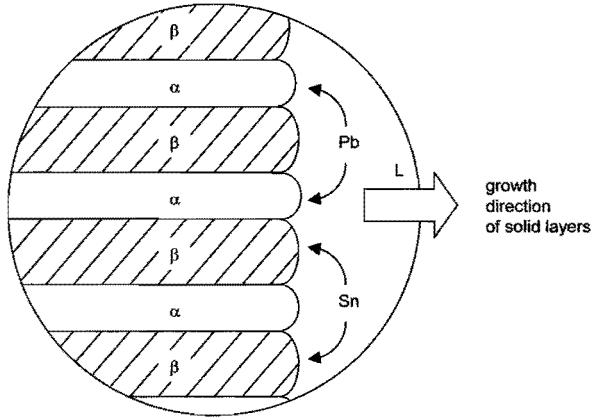


Figure 8.9. The layered eutectic structure is formed by sideways growth.

What will happen during cooling of a melt with a non-eutectic composition? That depends on whether we are at lower levels of tin, or higher ones. We will first look at a level of tin *below* the eutectic composition, e.g. 40 wt% Sn.

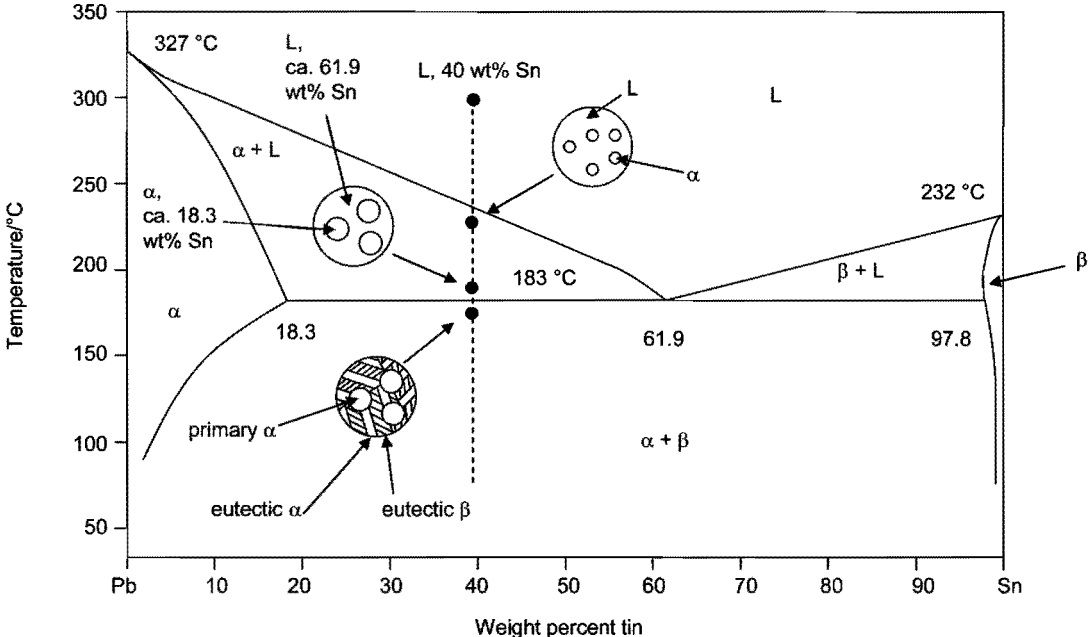


Figure 8.10. Cooling a melt of 40 wt% Sn.

As can be seen in Figure 8.10, the melt will be one phase (L) until ca. 230 °C, where we reach the forbidden zone " $\alpha+L$ ". Here, the material must separate into a solid (α) and a liquid (L): in the melt there will be grains of α with a composition of ca. 17 wt% Sn. Further cooling will give more solid α , and the compositions of both α and L will change, as given by the solidus and liquidus, respectively. Just above the eutectic, the solid phase that forms will have a composition of just below 18.3 wt% Sn, and the remaining liquid will be at just below 61.9 wt% Sn. At this temperature we can use the lever rule, to find that we have 50 wt% α and 50 wt% L.

Just below the eutectic line, we have a microstructure of the solid material with particles of α in a layered matrix of $\alpha+\beta$. All α phases (grains and layers) will have a composition of just below 18.3 wt% Sn, and all β layers have a composition of just above 97.8 wt% Sn. At this temperature we can use the lever rule to find a physical composition of 73 wt% α and 27 wt% β .

Further cooling will lead to further composition changes: the α phases will contain less and less Sn, while the β phases will get more and more Sn. Also, the quantities of the phases will therefore change according to the lever rule.

But when we start with a composition above the eutectic composition, e.g. 70 wt% Sn, we first pass through the $\beta+L$ region before we reach the eutectic. The final result is similar, except that we get particles of β in a eutectic matrix (try this yourself!). This will lead to quite different mechanical properties.

When we start at concentrations below 18.3 wt% Sn, we will never pass the eutectic line, and we will simply get formation of solid α from the melt, which at lower temperatures will give some small quantity of β solid particles embedded in an α -matrix, as shown in Figure 8.11.

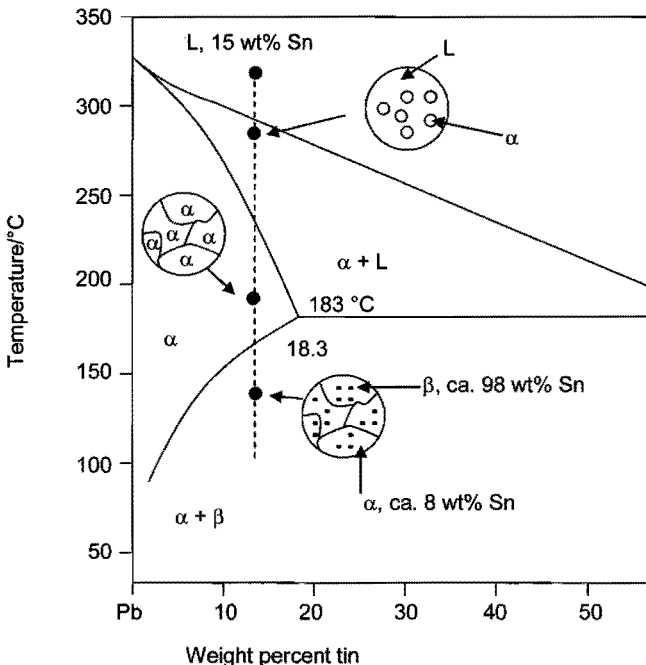


Figure 8.11. Cooling a melt of 15 wt% Sn.

For very low Sn-concentrations (almost pure lead), we will not even see solid β appear, but we can get pure α from the melt, since we never reach the $\alpha+\beta$ region.

8.2.2 Steel

For a realistic, well researched, and important example, we will look at the phase diagram of iron (Fe) and carbon (C). For practical purposes, we usually display this as the phase diagram of the components Fe (pure) and the very stable compound Fe_3C (6.67 wt% C), since this almost always forms instead of pure carbon (see Figure 8.12).

When the carbon content is low enough (< 2.14 wt%), the material we get is called **steel**, and is indeed built up from Fe and Fe_3C . For higher carbon contents (> 2.14 wt%), the material is called **cast iron**. Cast irons can also contain pure carbon as component, but we will not discuss these any further here. Cast irons can be molten more easily, but are very brittle.

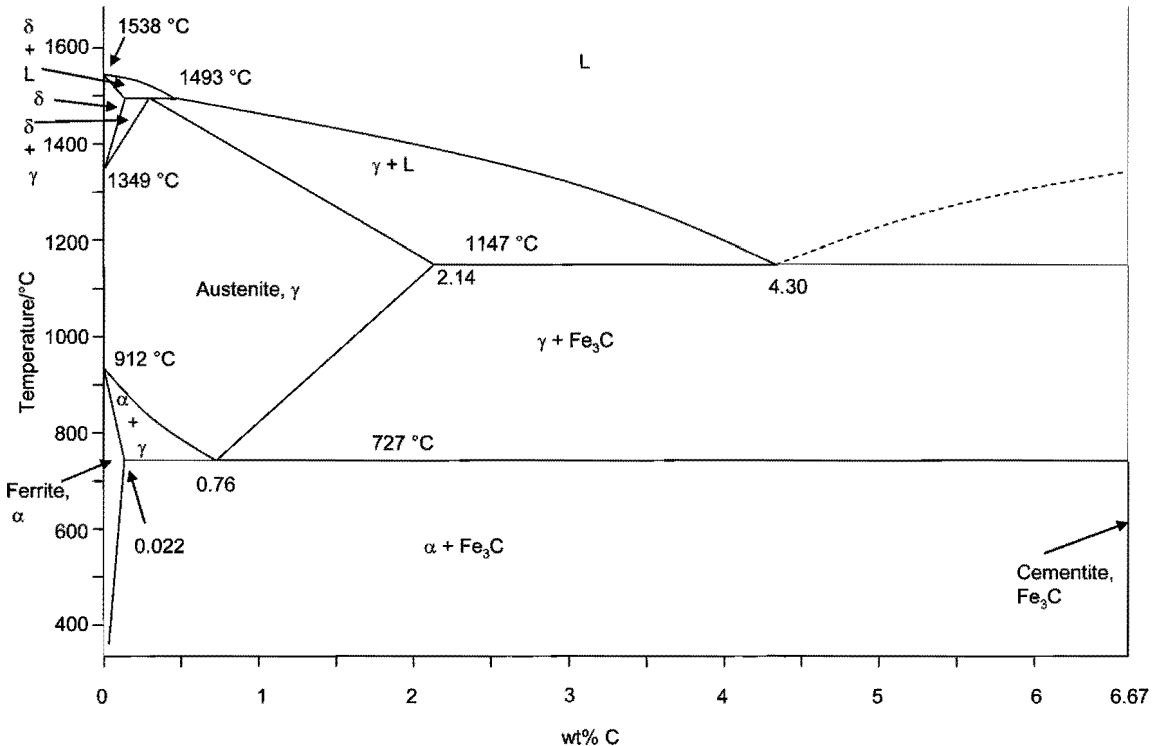


Figure 8.12. Phase diagram of iron (Fe) and cementite (Fe_3C).

In this phase diagram we see, besides the liquid melt (L), the following solid phases: α -Fe (**ferrite**, BCC metal), γ -Fe (**austenite**, FCC metal), δ -Fe and Fe_3C (**cementite**, brittle ceramic).

We will mainly look at the region of the diagram where austenite (γ) is cooled. This will in principle always give mixtures of ferrite (α) and cementite (Fe_3C), but the microstructure of the resulting material can be very different, since there is a eutectic line at 727 °C with the austenite composition at 0.76% C. Since ferrite is tough and

ductile, but cementite is hard and brittle, this can dramatically change the mechanical properties of the material.

Cooling austenite at exactly 0.76 wt% C (see Figure 8.13) will mean that other phases are formed for the first time on the eutectic line. There you simultaneously get α -Fe and Fe_3C , which form a lamellar material: **pearlite**. Due to the overall composition, you get plates of cementite in an α -Fe matrix, since more α -Fe will be formed (check this with the lever rule). Also here, the formation of the lamellar structure occurs by a “sideways” growth. The austenite was formed as grains from the original melt, and the new phases will be formed at the grain boundaries. Since ferrite is metallic, we get a ductile matrix with brittle ceramic plates in it.

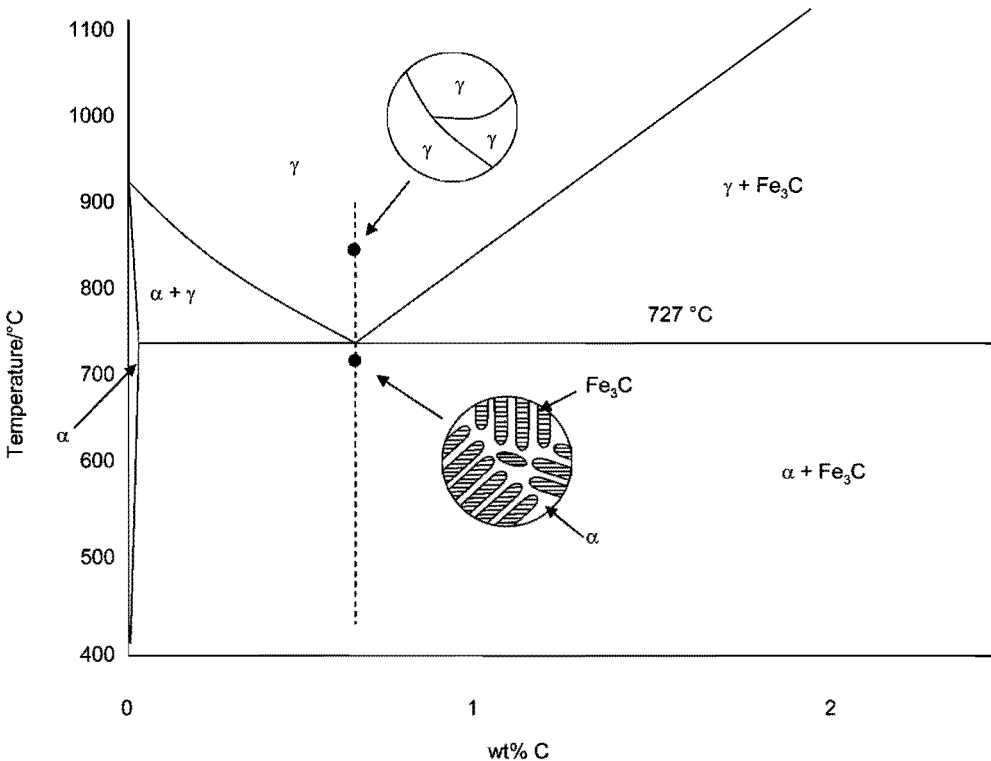


Figure 8.13. Cooling austenite at the eutectic composition, yielding cementite (dashed) and ferrite (white).

For an austenite with a composition below 0.76 wt% C, cooling takes us through the “ $\alpha + \gamma$ ” region (see Figure 8.14, left), so first α -Fe grains will be formed on the grain boundaries in the γ -Fe. This α -Fe will therefore later form the matrix of the final material. The last γ -Fe particles will disappear and form a eutectic mixture at 727 °C: pearlite (layers of α -Fe and Fe_3C). These pearlite particles will be embedded in a matrix of α -Fe. Since you now have a matrix of ductile ferrite, the material is not very strong (low σ_Y), but quite tough.

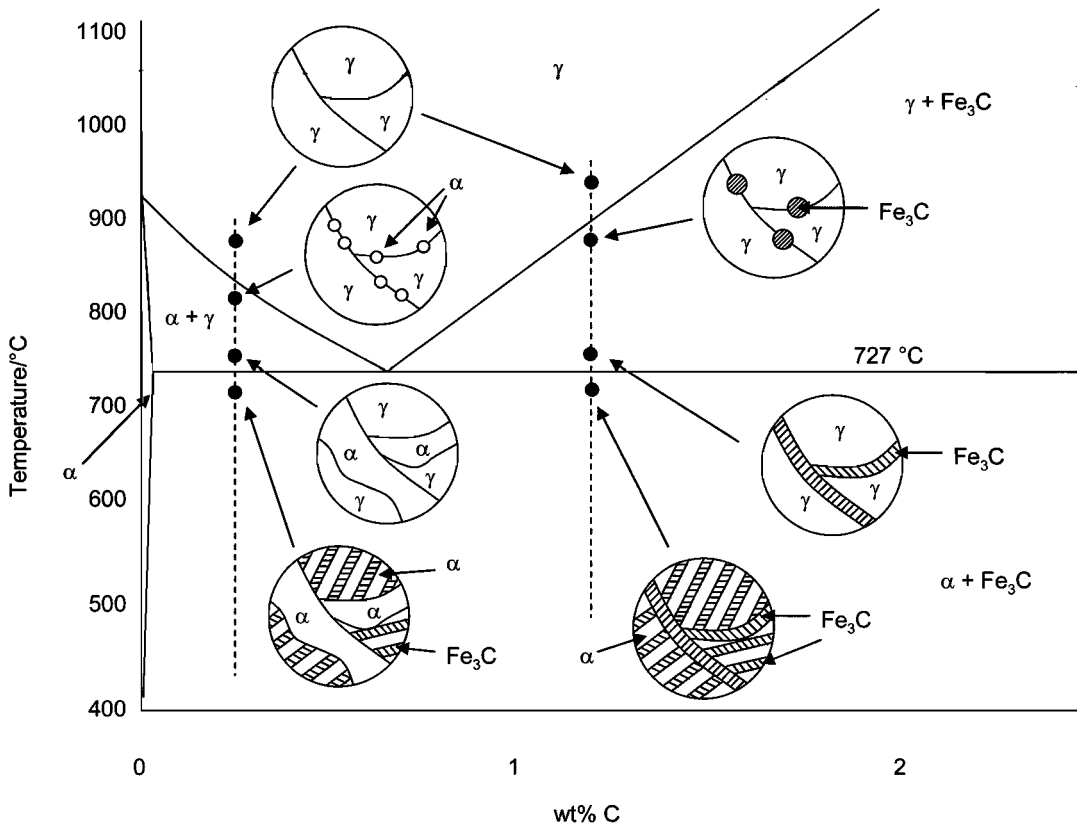


Figure 8.14. Cooling an austenite with less (left) and more (right) than 0.76 wt% C.

Austenite with more than 0.76 wt% C will pass through the “ $\gamma + \text{Fe}_3\text{C}$ ” region (see Figure 8.14, right), and first form Fe_3C grains on the grain boundaries in the γ -Fe. So, the matrix of the final material will be cementite. The last γ -Fe will disappear at the eutectic line, and we get pearlite particles in a cementite matrix. This gives a material with a very high yield stress, but it will break easily.

8.2.3 Kinetics*

Unfortunately, things do not always happen the way it is described by the phase diagram. Changes from one solid phase to another solid phase (e.g. $\gamma \rightarrow \alpha$) are normally quite slow, so we do not get the equilibrium structures.

One way of studying the effect of time is by keeping austenite at a certain fixed temperature below 727 °C, where it should change to ferrite and cementite, and see how long this takes. We then get a **TTT-diagram** (time–temperature–transformation), in which the solid lines indicate 1% and 99% transformation, and the dashed line is 50% transformation. Take care: the time scale in Figure 8.15 is logarithmic.

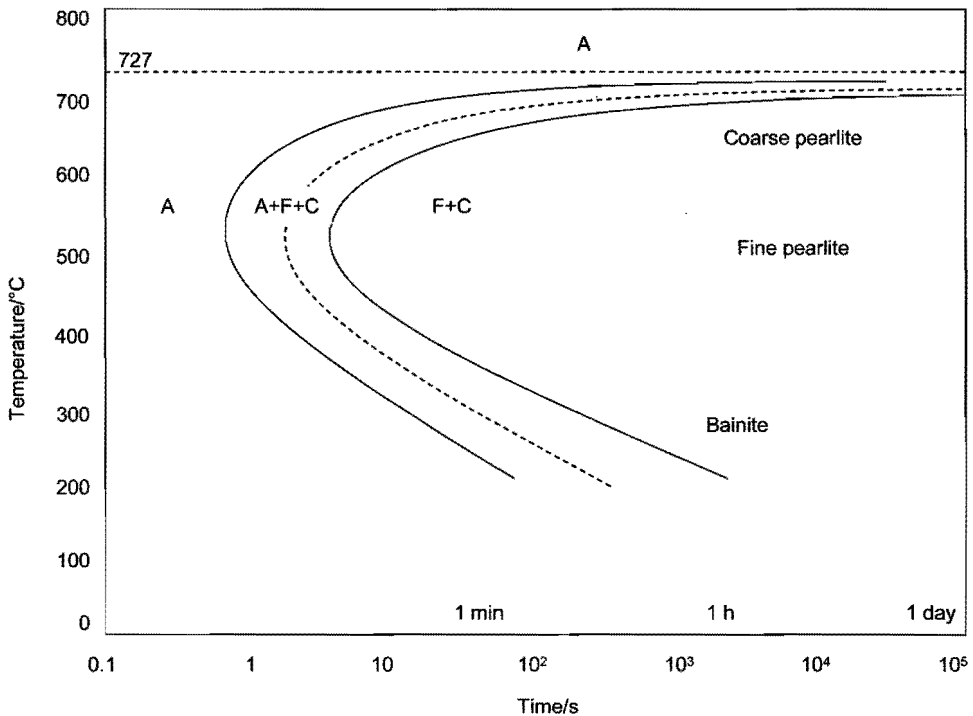


Figure 8.15. TTT-diagram for the cooling of austenite (A), forming ferrite (F) and cementite (C).

We can see several things in such a diagram. One of them is that it takes a long time to change the phases at high temperature and low temperature, but only a short time at medium temperature. Why is this?

At high temperature, there is little driving force to form another phase (we are just below the eutectic), and we will slowly get a few new grains, which will then grow larger. The final material is coarse pearlite: it contains large grains.

At low temperature the driving force is large (far below eutectic), but the processes in these solids are quite slow (diffusion). Now, we will get many grains formed, but they will grow very slowly. The final material is called **bainite**, with many small grains.

In between, we have an optimum combination of driving force and growth speed: we will get a medium amount of grains with medium size. This material is called fine pearlite. The microstructure becomes finer (more narrow layers) when we go from coarse pearlite via fine pearlite to bainite. This means that the strength will increase, but the toughness will decrease.

Another process occurs when we quickly cool (quench) austenite: we do not get pearlite at all, but **martensite** with a needle-shaped microstructure. This is formed without diffusion, which explains why it occurs so quickly. Martensite has a deformed crystal structure (body-centered tetragonal, BCT), which is actually not stable, but will slowly change into a cubic lattice (it is a metastable state). It is very hard, because the carbon content is actually too high for this crystal structure, so we get a lot of tension. This internal tension can even be too large for the material to withstand, and

we can get spontaneous fracture. Therefore martensite is often tempered (annealed), which releases some of the stress. We will then get the formation of cementite on the grain boundaries, thus reducing the carbon content. The material will then be less strong, but much tougher.

In practice, the TTT-diagram is often replaced by a **CCT-diagram** (continuous-cooling-transformation), since continuous cooling at a certain speed is more realistic than annealing at constant temperature (Figure 8.16).

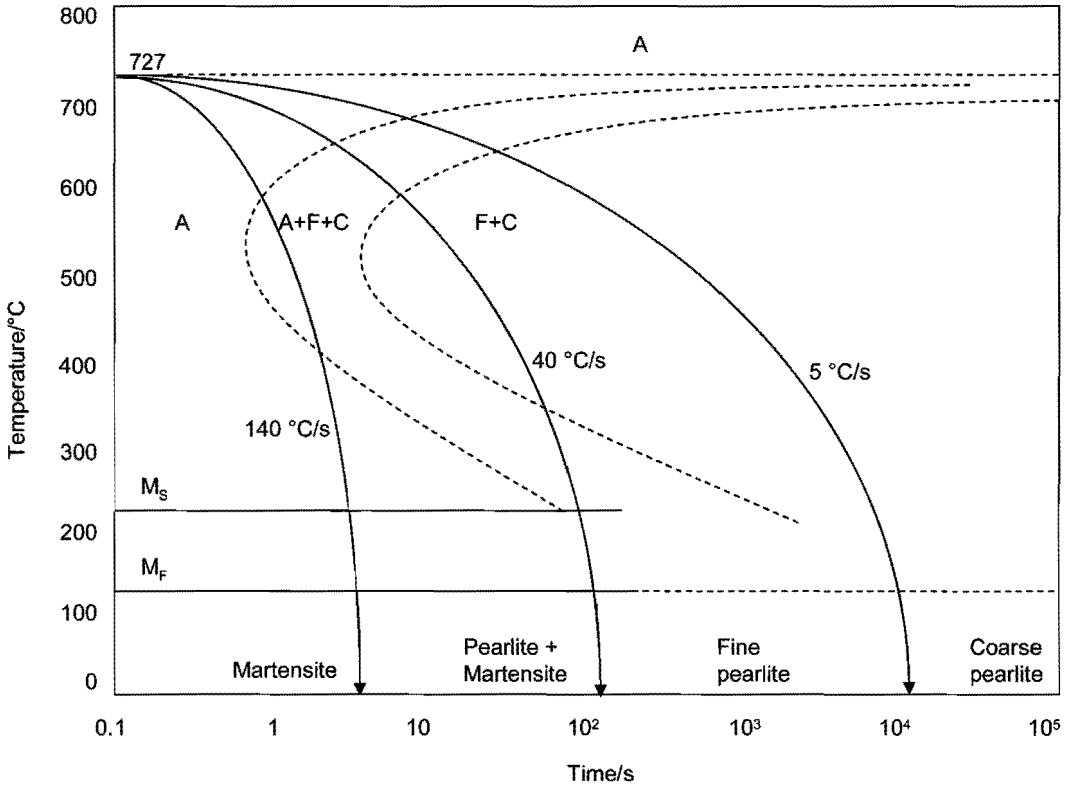


Figure 8.16. CCT-diagram for the cooling of austenite. M_s indicates the start and M_f the completion of martensite formation.

The quicker you cool, the harder the steel that is formed: you can get almost completely martensite instead of pearlite or bainite. By adding small amounts of other metals, the change to pearlite can be slowed down further, and normal cooling will still give you martensite.

So, the general conclusion is: although phase diagrams are very useful for predicting microstructures, the kinetics of the processing technique must not be forgotten.

8.3 Polymers

In polymeric materials, the mechanical properties are strongly determined by the mobility and orientation of the macromolecules. Both these factors are determined by the interactions between the macromolecules, and therefore by their chemical structure. Since we can make copolymers, we can combine different chemical structures in one macromolecule. This is necessary, since most polymers of different chemical composition do not mix easily.

By now making block-copolymers, large blocks of different chemical composition can be combined into one material. Often, the blocks of similar properties will cluster together (no mixing): we get a kind of phase separation on a very small scale (nanometers). This is often called microphase separation.

In addition, the different chemical blocks in the macromolecules can form amorphous and crystalline parts, which can further increase the possibilities for combining mechanical properties in a material.

Actually, you have now made a composite material, with e.g. hard blocks in a soft matrix. The volume fractions of both parts can be adjusted via the synthesis, and this will lead to different microstructures, and therefore to different mechanical properties. Low amounts of one block lead to the formation of spherical phases of that block in a matrix of the other block. Longer blocks lead to cylinders in a matrix, and equal lengths of the blocks give a lamellar structure.

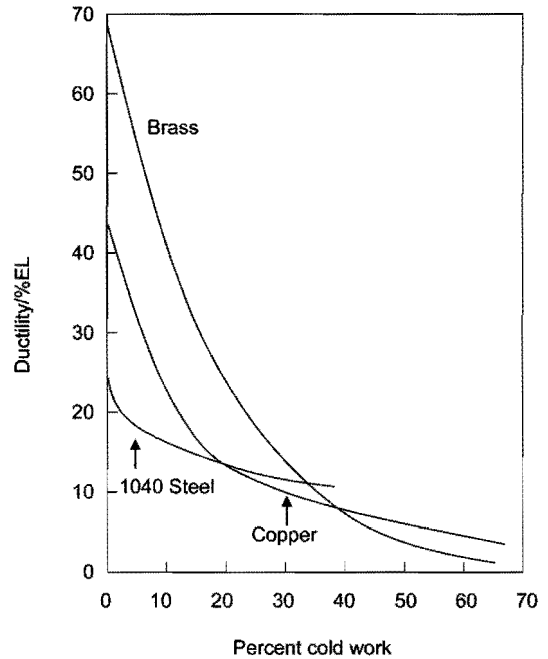
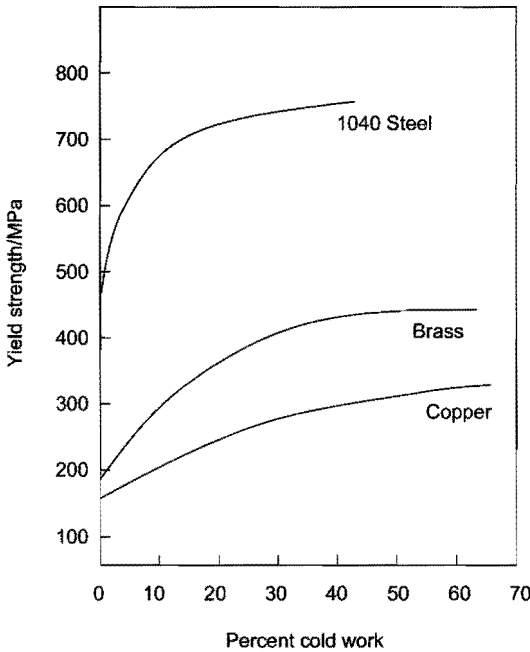
For block-copolymers we get a special behaviour at the surface of the material: the blocks of the macromolecule with the lowest surface energy (γ) will be present much more on the surface. This means that the material presents a quite different surface to the environment than one would expect based on the average (bulk) composition. Of course, the same can happen for the various additives that are usually added to polymeric materials in small quantities: they can aggregate at the surface, and have a much larger effect than expected.

Another possibility to change the mechanical properties of a polymeric material is by stretching it: this leads to a more parallel orientation of the macromolecules, which thereby get stronger interactions. This can lead to very strong fibres, since ultimately there are only covalent bonds in the draw direction.

Problems

8.1. A cylindrical specimen of cold-worked Cu has a ductility of 25 %EL. If its cold-worked radius is 10 mm, what was its radius before deformation?

Note: In the figures below, cold working is indicated as: $\%CW = 100(A_0 - A_{final})/A_0$



8.2. A cylindrical rod of Cu, originally 16.0 mm in diameter, is to be cold-worked by drawing; the cross section will remain circular during deformation. A cold-worked yield strength of 250 MPa and a ductility of 12 %EL are desired. Furthermore, the final diameter must be 11.3 mm.

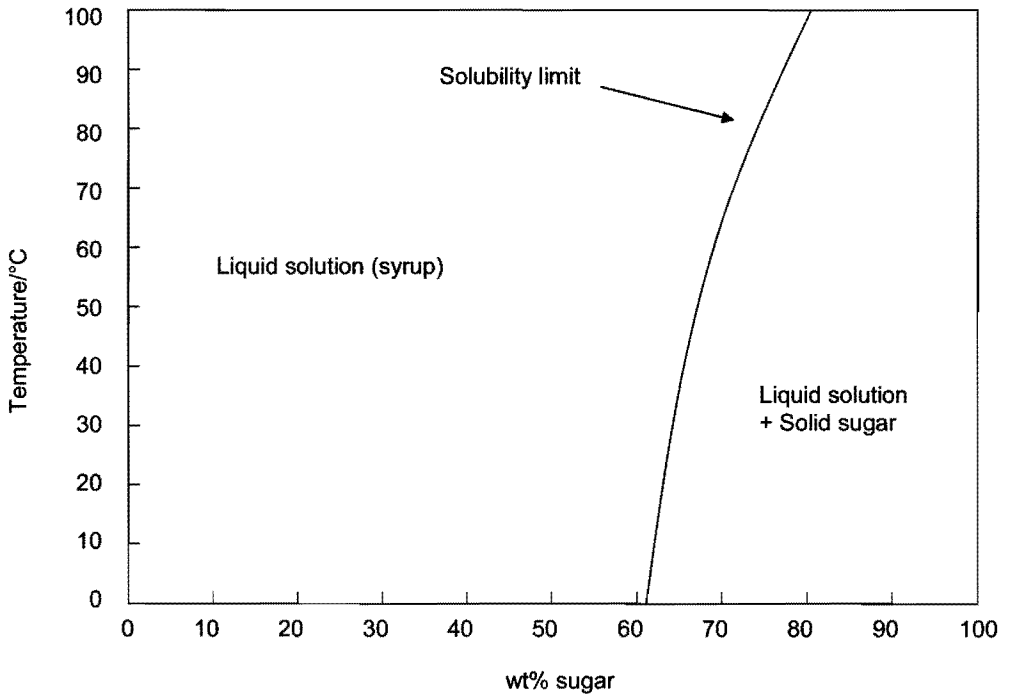
Explain which subsequent processing steps must be followed to accomplish this.

Hint: It can not be done in 1 processing step!

8.3. To get weight savings, a steel is quenched and tempered, strengthening it from 100 MPa, where K_{1C} is $76 \text{ MPa}\cdot\text{m}^{1/2}$, to 2000 MPa, where $K_{1C} = 26 \text{ MPa}\cdot\text{m}^{1/2}$. What change in the critical crack length for brittle fracture occurs for a design stress of 800 MPa?

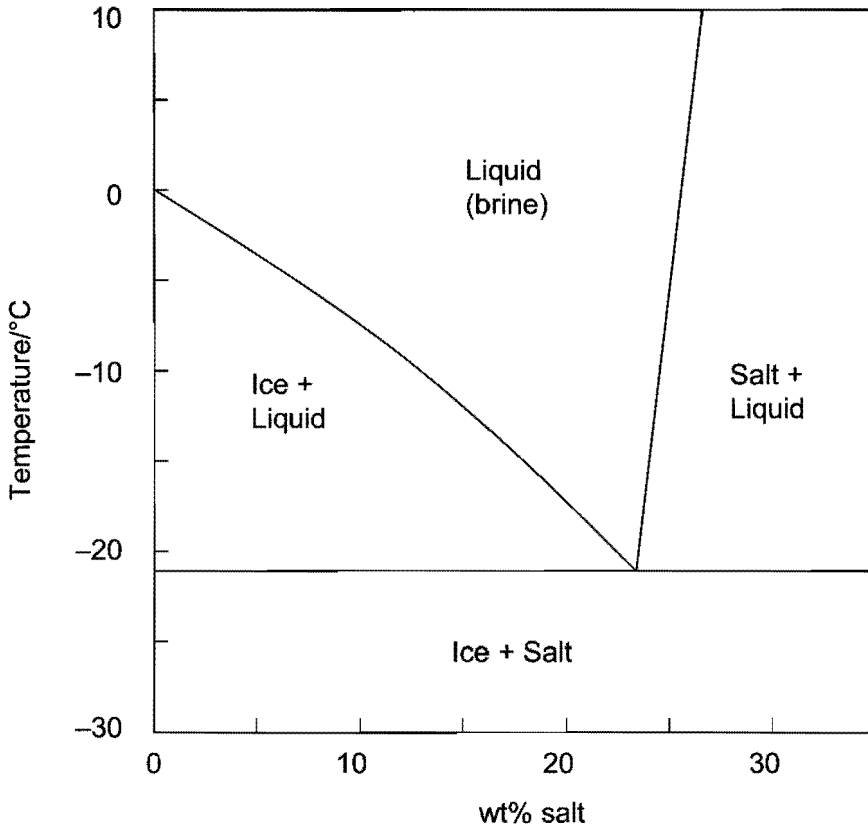
8.4. The yield point for an iron that has an average grain diameter of 0.05 mm is 135 MPa. At a grain diameter of 0.008 mm, the yield point increases to 260 MPa. At what grain diameter will the yield point be 205 MPa?

8.5. Consider the sugar–water phase diagram:



- How much sugar will dissolve in 1500 g water at 90 °C?
- If the saturated solution in part a. is cooled to 20 °C, some of the sugar will precipitate. What will be the composition of the saturated sugar solution in wt% sugar) at 20 °C?

8.6. Below is a portion of the H_2O – NaCl phase diagram.

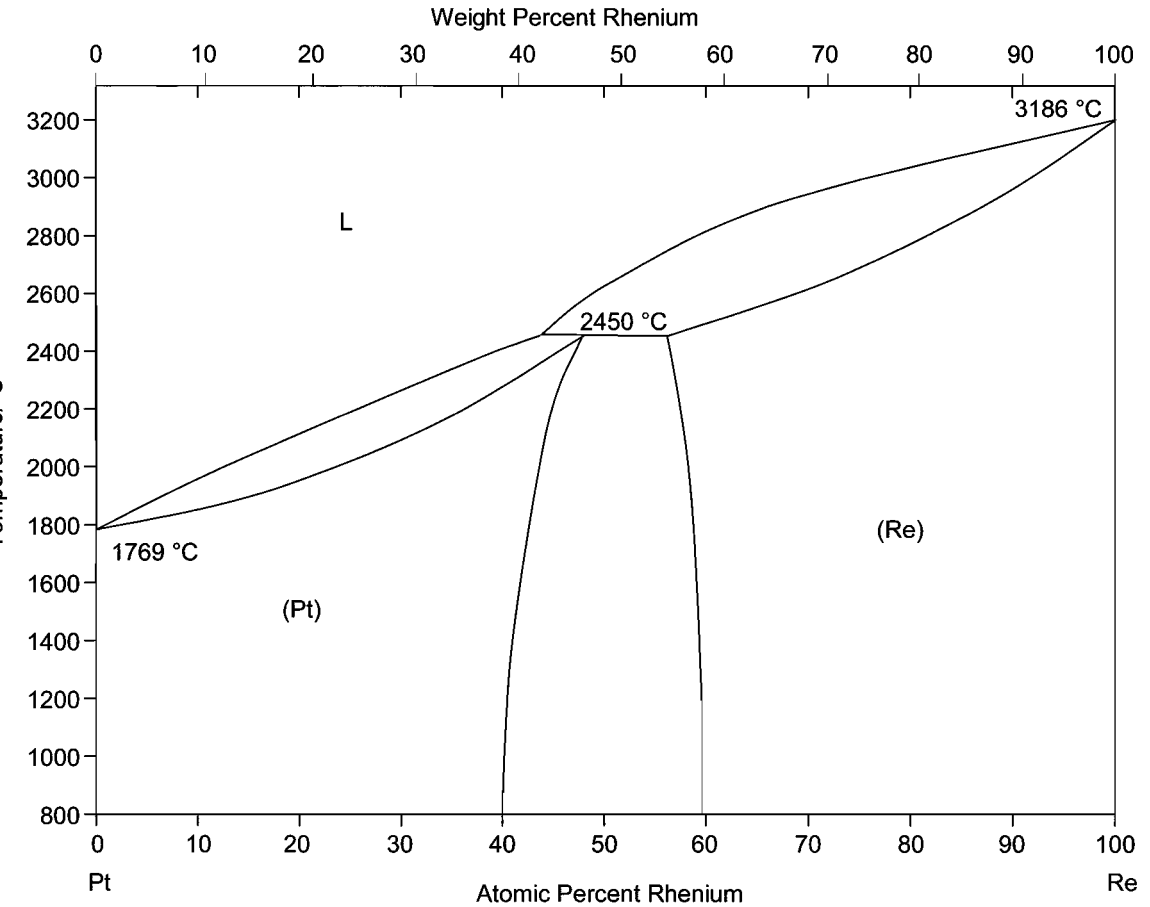


- Using the diagram, explain how spreading salt on ice below 0 °C can cause the ice to melt.
- What concentration of salt is necessary to have brine with 50 wt% ice and 50 wt% liquid at -10 °C?

8.7. A 90 wt% Sn–10 wt% Pb alloy is cooled from 300 °C to 0 °C.

- What is the composition of the alloy in terms of molar percentages?
- Upon cooling of this alloy, the number of degrees of freedom changes from 2 to 1 to 0 to 1. List possible temperatures that correspond to these four conditions.
- In what way does the equilibrium microstructure of this alloy differ from that of 90 wt% Pb–10 wt% Sn?

8.8.* Consider the 50 wt% Pt–50 wt% Re alloy. This alloy is heated to 2800 °C and then cooled to 800 °C. Perform complete equilibrium chemical and physical phase analyses at 2800, 2452, 2448, and 1000 °C during the cooling process. The Pt-rich phase (Pt) is usually called α , and the Re-rich phase (Re) is usually called β .



8.9. Cast iron weighing 1 kg and containing 3.5 wt% C (remainder Fe) is melted and slowly cooled from 1400 °C.

- a. Perform complete phase analyses just below 1147 °C, at 900 °C, and just below 727 °C.
- b. Sketch the expected microstructure at 500 °C.

8.10. The solid-state transformation from austenite to pearlite follows the Avrami equation, where y is the fraction converted and t is the time:

$$y = 1 - e^{-kt^n}$$

It is found that $y = 0.2$ at 12.6 s, and $y = 0.8$ at 28.2 s. Determine the total time required for a conversion of 95%.

9 **Changing material properties II: (Bio)composites**

Composites can combine the best properties of two or more materials. A usual combination is an inorganic material (metal, ceramic) with an organic material (polymer) in order to combine strength and toughness.

Do not go upon what has been acquired by repeated hearing; nor upon traditions; nor upon rumour; nor upon what is in scripture;...nor upon the consideration, "The monk is our teacher".

Siddhartha Gautama, "Buddha" in the Kālāma Sutta
(c. 563–c. 483 BCE)

9.1 Structure

Composites of two materials are found in all possible combinations of metals, ceramics, and polymers.

However, one of the most important factors for the properties of a composite is the way the two materials are combined: are they just mixed at random, or is there an ordered structure? Especially in biocomposites we will find a highly optimized structure due to selection during evolution, building up by growth, and adaptation to the surroundings during their functioning.

For synthetic composites, the most common types of structures are: *particles* in a matrix, **fibres** in a matrix, and alternating *layers*. For fibres, there are differences between short and long fibres, and also the orientation of the fibres is quite important. In fact, **particulate** composites have much in common with materials that were obtained by precipitation hardening (see Chapter 8). Fibre-reinforced materials are often easy to make, and are very important nowadays. **Laminar** materials are more difficult to produce.

9.2 Mechanical properties

9.2.1 Stiffness

The modulus of a composite is dependent on the volume fraction of particles, fibres or layers of the components, and also on the orientation of the fibres or layers. There are two extreme cases that are easy to describe (Figure 9.1):

- fibres or layers *parallel* to the applied force: the **Voigt** or **isostrain** model;
- fibres and layers *perpendicular* to the force: the **Reuss** or **isostress** model.

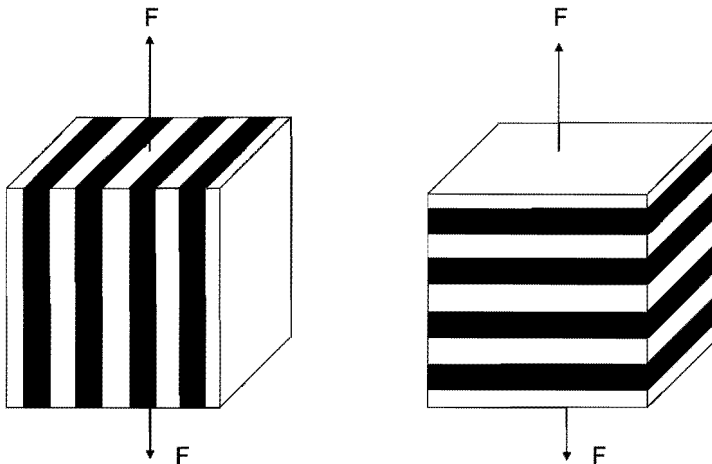


Figure 9.1. Left: Voigt model for composites; right: Reuss model.

The behaviour of most composites is in between these extremes, so we can predict a range for the stiffness between the outcomes of the two models.

Voigt or isostrain model

For materials that are parallel (layers or fibres parallel to the force) the strains must be equal:

$$\varepsilon = \varepsilon_1 = \varepsilon_2$$

However, now the two components will feel different stresses, dependent on the surfaces they present to the force:

$$F_1 = \sigma_1 A_1 = E_1 \varepsilon A_1 \qquad F_2 = \sigma_2 A_2 = E_2 \varepsilon A_2$$

In total the force carried by the composite is:

$$F = F_1 + F_2 = \varepsilon(E_1 A_1 + E_2 A_2) = \varepsilon EA$$

This means for the total stress:

$$\sigma = \varepsilon \left(E_1 \frac{A_1}{A} + E_2 \frac{A_2}{A} \right)$$

We now define the volume fractions in the following way:

$$V_1 = \frac{A_1}{A} \qquad V_2 = \frac{A_2}{A}$$

We then get:

$$\sigma = \sigma_1 V_1 + \sigma_2 V_2 \qquad \text{or:} \qquad E = V_1 E_1 + V_2 E_2$$

When one of the components has a much higher modulus ($E_1 \gg E_2$), then this component now determines the modulus of the composite ($E \approx V_1 E_1$). This component will also carry most of the force ($F \approx F_1$ or: $\sigma \approx V_1 \sigma_1$).

Reuss or isostress model

For materials in series (e.g. two layers perpendicular to the force), we must have the same stress for both components:

$$\sigma = \sigma_1 = \sigma_2$$

However, each of the components has a different deformation:

$$\varepsilon_1 = \frac{\sigma}{E_1} = \frac{\Delta L_1}{L_{1,0}} \qquad \varepsilon_2 = \frac{\sigma}{E_2} = \frac{\Delta L_2}{L_{2,0}}$$

The total strain is then:

$$\varepsilon = \frac{\Delta L}{L_0} = \frac{\Delta L_1 + \Delta L_2}{L_{1,0} + L_{2,0}} \neq \varepsilon_1 + \varepsilon_2$$

We can introduce the volume fractions of the two materials with:

$$V_1 = \frac{L_{1,0}}{L_0} \quad V_2 = \frac{L_{2,0}}{L_0}$$

Then we see:

$$\varepsilon = V_1 \varepsilon_1 + V_2 \varepsilon_2 = V_1 \frac{\sigma}{E_1} + V_2 \frac{\sigma}{E_2} = \frac{\sigma}{E}$$

So, there is an effective modulus for the composite of:

$$E = \frac{1}{\frac{V_1}{E_1} + \frac{V_2}{E_2}} \quad \text{or:} \quad \frac{1}{E} = \frac{V_1}{E_1} + \frac{V_2}{E_2}$$

When one of the layers has a much higher stiffness ($E_1 \gg E_2$), then the composite modulus is determined by the component with the lowest stiffness ($E \approx E_2/V_2$).

9.2.2 Strength

The fracture strength of a fibre-reinforced composite is dependent on whether we have long (continuous) or short fibres.

For *long* fibres, the fibres must be broken, and we can estimate the strength by combining the tensile strength of the fibres ($\sigma_{T,f}$) and the yield strength of the matrix ($\sigma_{Y,m}$) via the appropriate volume fractions:

$$\sigma_{T,c} = V_f \sigma_{T,f} + V_m \sigma_{Y,m} \quad \text{continuous fibres.}$$

For *short* fibres, fracture is determined by how well the fibres stick to the matrix (shear stress τ_{fm}). There is an optimum length for the fibres: too short and they break too quickly, too long and it is a waste of fibre material because they are not carrying more load. Suppose we have a cylindrical fibre with diameter d_f , then at an inserted length x the area between fibre and matrix is $\pi x d_f$, and the total shear force is:

$$F = \pi d_f \tau_{fm} x$$

The force where the fibre breaks is determined by the cross-sectional area ($\pi d_f^2/4$):

$$F = \sigma_{T,f} \pi d_f^2/4$$

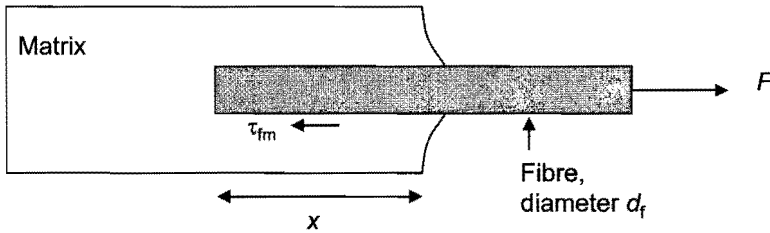


Figure 9.2. Forces on a fibre in a matrix.

When the total shear force equals the breaking force, we have arrived at the critical length x_c :

$$x_c = \frac{\sigma_{T,f} d_f}{4\tau_{fm}}$$

When the fibres are stressed from both ends, as in the middle of a matrix, the stress is maximal in the centre of the fibre. Again, the optimum length of the fibre is reached when the maximum stress reaches the fibre tensile strength. This is twice the critical length we just derived:

$$L_{opt} = \frac{\sigma_{T,f} d_f}{2\tau_{fm}}$$

Longer fibres do not carry more load (they simply can not), so the extra fibre is wasted. Shorter fibres do not carry the maximum possible load, so the composite could be stronger.

It is now possible to calculate the tensile strength of the composite for short fibres (the details are not shown here). For short fibres that are longer than the optimal length ($L > 2x_c$), we get:

$$\sigma_{T,c} = \sigma_{T,f} V_f \left(1 - \frac{x_c}{L}\right) + \sigma_{Y,m} V_m \quad V_m = 1 - V_f$$

When L becomes very large, we get the formula for continuous fibers (check this!).

For the optimum length fibres ($L_{opt} = 2x_c$), we get from this formula:

$$\sigma_{T,c} = \frac{1}{2} V_f \sigma_{T,f} + V_m \sigma_{Y,m} \quad \text{Korte van optimale lengte.}$$

When the fibres are shorter than the optimum length ($L < 2x_c$), the result is quite different:

$$\sigma_{T,c} = \frac{L\tau_{fm}}{d_f} V_f + \sigma_{Y,m} V_m$$

However, for the optimum length, we still get the same strength (check this!).

9.2.3 Toughness

A composite's main advantage is that it is virtually always tougher than the materials it is made of. In a composite, a growing crack will stop at the interface of the two components. The crack will follow the interface between the materials, instead of growing into the second component, so the crack will be deflected (see Figure 9.3).

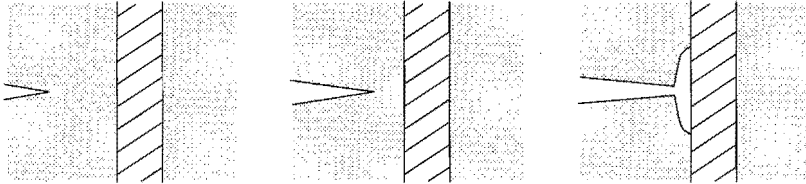


Figure 9.3. A crack in a composite can not grow straight.

Also in particulate composites, we can e.g. use rubber particles that must be torn open (absorbing a lot of energy) for a crack to grow further.

Of course, when the fibres are oriented, there will be a dependence of the fracture strength on the direction of the applied force (see Figure 9.4): forces parallel to the fibres can lead to breaking of the fibres, while perpendicular forces will lead to breaking of the matrix. Finally, shear forces can lead to slipping of the fibres through the matrix.

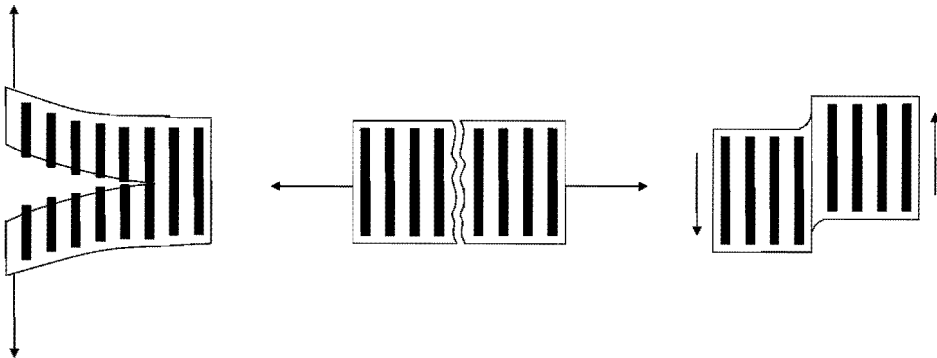


Figure 9.4. Fracture in oriented-fibre composites by tensile forces parallel (left) and perpendicular (middle) to the fibres, and by shear forces (right).

We can calculate the work of fracture for a fibre-reinforced composite, again differentiating between long and short fibres (the details will not be shown here).

For *short* fibres ($L < 2x_c$), which will be drawn out of the matrix, the interaction strength between fibre and matrix (τ_{fm}) is important:

$$W_f = \frac{\tau_{fm} V_f L^2}{2d_f}$$

For long fibres ($L > 2x_c$), the breaking of the fibres will be more important:

$$W_f = \frac{\sigma_{T,f}^2 V_f d_f}{8\tau_{fm}}$$

9.2.4 Fibres

Nowadays very strong fibres can be made, such as Ultra-high molecular weight poly(ethylene) (UHMWPE or Spectra), buckytubes (C-nanotubes) and diamond fibres. C-nanotubes in theory have an ultimate tensile strength of 300 GPa, and a maximum strain of 30%. Experimentally a tensile strength of 30 GPa has already been found, and a strain of 12%. For the Young's modulus values of ca. 1000 GPa have been observed. Take a look at Appendix C (Example 2) why this might be interesting.

The strongest fibers have a specific tensile strength of almost 4 MPa/(kg·m⁻³), and the specific Young's modulus can reach almost 250 MPa/(kg·m⁻³). Both values are about 10 times higher than those for strong metals like steel or titanium alloys.

9.2.5 Composites as biomaterials

Composites are being used in a variety of functions, e.g. implants in joints and heart valves. Examples are:

- C-fibres in a C-matrix: very strong, but hard to produce;
- PMMA with hydroxyapatite and glass-ceramics as bone cement;
- PE with hydroxyapatite as bone replacement;
- polymers with quartz as tooth replacement;
- polymers and ceramics with drugs encapsulated for controlled drug delivery;
- polymers with C- or glass fibres;
- Bioglass with metal (steel, Ti) fibres;
- Collagraft: small (mm-sized) ceramic crystals of a mixture of hydroxyapatite and tricalcium phosphate in a collagen matrix; used for bone repair;
- polyurethane with fibreglass as cast material for broken bones.

9.3 Biocomposites

9.3.1 Keratin

We have already talked about this material in Chapter 7: it is a semi-crystalline protein that occurs in hair, nails, and the top layer of the skin (the stratum corneum or horny layer of the epidermis). The amorphous matrix is heavily crosslinked, but does show yield. Because of this, the fracture strength (up to ca. 1 GPa) is independent of the size of notches on the surface. This is highly useful for the nails and horns that are built up mainly from keratin.

The stiffness of this composite can be calculated with the models we discussed earlier: the crystalline fibres have a modulus $E_f = 6.1$ GPa, and the matrix has $E_m = 6.1$ GPa in dry condition, $E_m = 3.1$ GPa in fresh condition (20% water), and $E_m = 0.9$ GPa in wet condition (40% water). The volume fractions of the two components are also dependent on the amount of water: $V_f = 61\%$, 56% , or 53% for dry, fresh, and wet, respectively (and of course: $V_m = 39\%$, 44% , or 47%).

The Voigt model with very long fibres now gives: $E_c = 6.1$ GPa, 4.8 GPa, and 3.6 GPa for dry, fresh, and wet, respectively.

Experimentally it is found that $E_c = 6.1$ GPa, 4.3 GPa, and 1.8 GPa (dry, fresh, wet). A better agreement is found with 40-nm long fibres: $E_c = 6.1$ GPa, 3.8 GPa, and 1.9 GPa for dry, fresh, and wet.

9.3.2 Soft tissues

In general these are **connective tissues** such as cartilage and tendon, and the connective tissues around muscles and nerves. Also, part of the skin is a soft tissue. Soft tissues consist of collagen fibres in a matrix of polysaccharides and proteins (the matrix is also called "ground substance"). Usually this combination is hydrated. Often there is a fixed ratio between the collagen and the charged polysaccharides, because the interaction between charged side groups stabilizes the collagen triple helix. These tissues also contain lots of cells, and undergo growth adaptation and repair.

First we will introduce some general terms that will be used a lot. Glycosaminoglycan (GAG) has already been mentioned in Chapter 6: polysaccharides with charged groups. **Proteoglycan** is a combination of protein and GAG, linked by covalent bonds. When there is no covalent bond, but only hydrogen bonding or electrostatic interactions, we call it a **protein-polysaccharide complex**.

A model that is used a lot to describe soft tissues is the **lamp brush** model (see Figure 9.5): collagen fibres in a matrix of proteoglycan and hyaluronic acid (a GAG). Collagen fibres are quite stiff ($E = 1$ GPa), and can be stretched elastically up to ca. 4%. At strains of 8–10% the fibres break.

The orientation and length of the fibres is also for these biocomposites very important: the fibres can be present in a parallel, crossed or random orientation, and they can be short (discontinuous) or can cross the whole material (continuous).

The matrix usually behaves like a visco-elastic paste that lubricates the fibres in their movements, and can carry some stress itself.

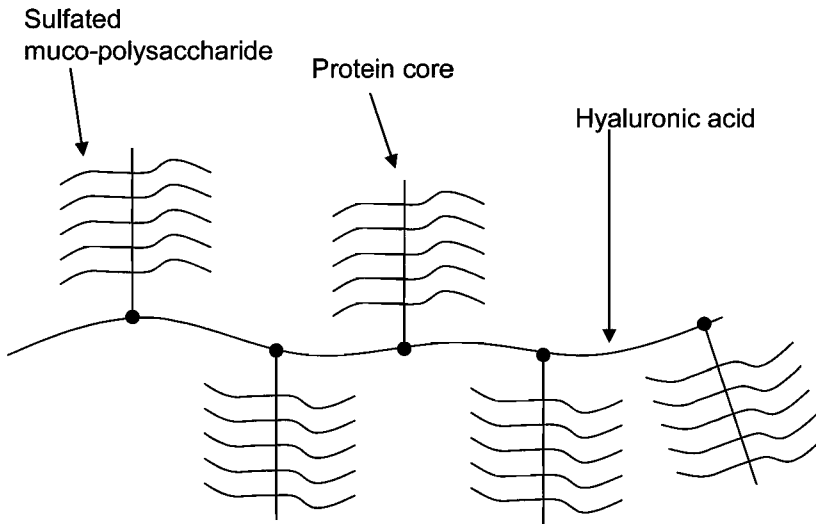


Figure 9.5. The “lamp brush”: the matrix around the collagen fibres is a core of charged sugars, decorated with proteins carrying charged sugars.

An important property of biocomposites is the Poisson ratio (ν): this can vary strongly, and is often anisotropic (direction-dependent). It is often assumed that $\nu = 0.5$ (no volume change), but for e.g. udder skin, we find $\nu = 1$, for arterial vessel wall we see $\nu = 0.3$, and for the membrane of a pregnant locust we can even get variation between 1 and 0, as seen in Figure 9.6.

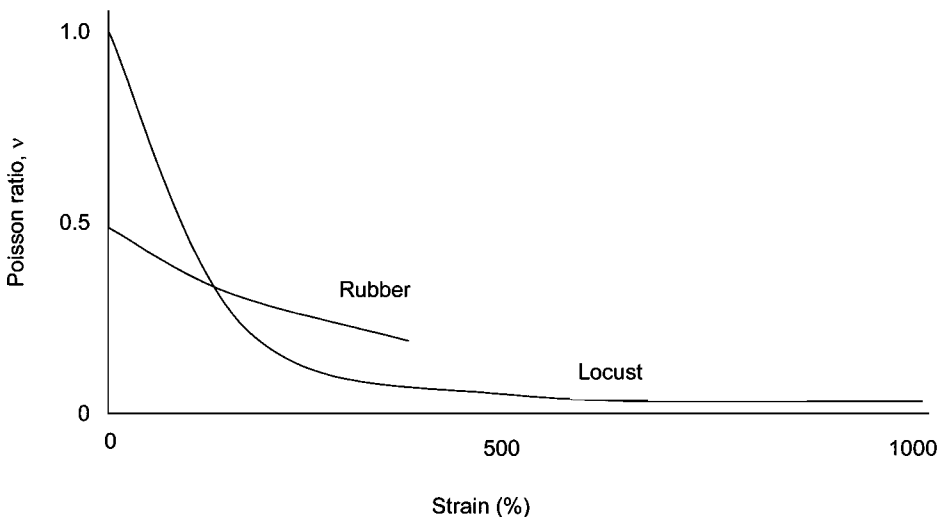


Figure 9.6. Variation of the Poisson ratio during stretching of rubber and locust membrane.

Mesoglea

A simple example of a soft tissue is the wall of the sea anemone *Metridium senile*: it consists of 6.7% collagen, 2% matrix, 86% water, and 5% salts.

The matrix is built up from neutral polysaccharides with proteins, and forms a rubbery gel with 2.4% solids. The salts screen the electrostatic interactions, which makes the gel more mobile than in the case of salt-free water.

The collagen fibres are discontinuous and oriented parallel. They give the mesoglea its strength, and lead to delayed reactions during viscous deformation.

Mesoglea can (slowly) be deformed elastically up to 200% strain with a modulus E of ca. 1 kPa. During rapid deformation, the material is more rigid (higher E). It costs ca. 1.2 kJ/m² to tear mesoglea, which is comparable to rubber.

Cartilage

Cartilage is a very special type of connective tissue, which contains a large amount of water. It consists of 15–25% collagen, 1.5–10% GAG (mostly chondroitin-sulphates), and 65–80% water. Sometimes there are some elastin fibres present (protein rubber). Hyaline cartilage is found on the surface of joints, between the ribs and the breast bone (costal cartilage), and in the trachea. It is mostly subjected to compression and shear forces. Fibrous cartilage is seen in the connections between bone and muscle, in intervertebral discs, and in the pelvis. It is mostly subjected to stretching, bending and twisting forces.

One of the building blocks of the matrix is **PPL** (2000–4000 kg/mol = 2–4 MDa), which has a protein core of 400 nm length, to which side chains of 60–100 polysaccharides are attached, each 100 nm long (50 kg/mol). Because the polysaccharides are negatively charged, they repel each other and are directed outwards. Therefore, the structure fills a very large volume ($R_g = 140$ nm). These PPLs aggregate via electrostatic interactions to larger complexes (50 MDa) according to the lamp brush model.

In cartilage, the collagen fibres form a network *around* the gel, leading to an osmotic pressure inside the material (ca. 0.35 MPa) which gives stiffness to the structure. It has been compared to a finely woven bag with jelly inside. As an example, here are the several nested layers of collagen fibres with different orientations in an intervertebral disc (see Figure 9.7).

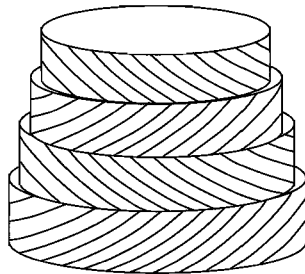


Figure 9.7. Structure of an intervertebral disc, with orientations of collagen shown.

Under stress, cartilage first responds elastically with a high stiffness, but after some time fluid starts leaking out, and there is stronger plastic deformation. When the

stresses are removed, the opposite happens: there is a quick elastic recovery, followed by slow recovery due to leaking of fluid into the material.

After a long wait, one finds values like $E = 16$ MPa for cartilage in the ribs, and fracture occurs at a strain of 8% (stretching), or yield is found at a strain of -6% (compression). Because of this behaviour, cartilage can function as an elastic buffer between other tissues.

Skin

Skin is a layered system: there is a hard outer layer (the **epidermis** of ca. $100\ \mu\text{m}$), which contains a lot of keratin, and a **dermis** (2–3 mm), which is a composite of collagen fibres in a protein–polysaccharide matrix, also containing some elastin fibres. Below this is the hypodermis, which contains a lot of adipose tissue (fat cells). This layer is used for heat isolation, energy storage, and as elastic cushion for the bones inside. Also, the collagen fibres in this layer, although there are fewer, are connected to the connective tissue below the skin.

The mechanical properties of skin are mainly determined by the dermis, so we will concentrate on that (dermis also gives strength to leather).

In the dermis, most collagen fibres are continuous through the matrix. Usually, fibres will orient in such a way that they are parallel to the local stress that the skin usually feels. There is no fixed orientation for the whole skin.

The matrix contains dermatan sulphate, bound to collagen fibres, and hyaluronic acid between the fibres.

Because of the elastin fibres, skin behaves like a rubber at low deformations (up to $\lambda = 1.6$). At larger strains ($\lambda = 1.9$) the collagen fibres become oriented in a parallel fashion, and then skin behaves more like tendon (see Figure 9.8).

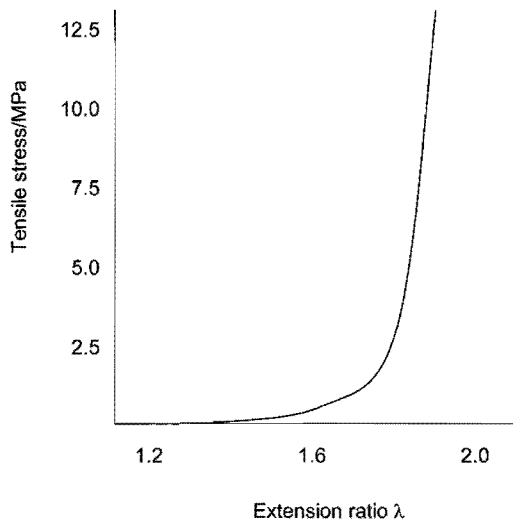


Figure 9.8. Tensile behaviour of skin.

In its normal condition, skin is pre-stressed to $\lambda = 1.1$ – 1.3 , which means that compression of skin initially only leads to relaxation of the elastin fibres (try it!).

Skin has a very high tear energy (toughness) of $20\ \text{kJ/m}^2$, and a stiffness of 100 MPa at high strains.

Tendon

Tendon is a composite connective tissue that is mainly built up from continuous, parallel collagen fibres (70–80% of the dry mass) with a matrix of cells, other proteins, polysaccharides, and salts. The matrix also contains 53% water.

Tendon can be stretched elastically to a strain of 4%, and then deforms irreversibly up to a strain of 8–10%. At the beginning of the σ, ϵ -curve (see Figure 9.9) there is a modulus $E = 1$ GPa.

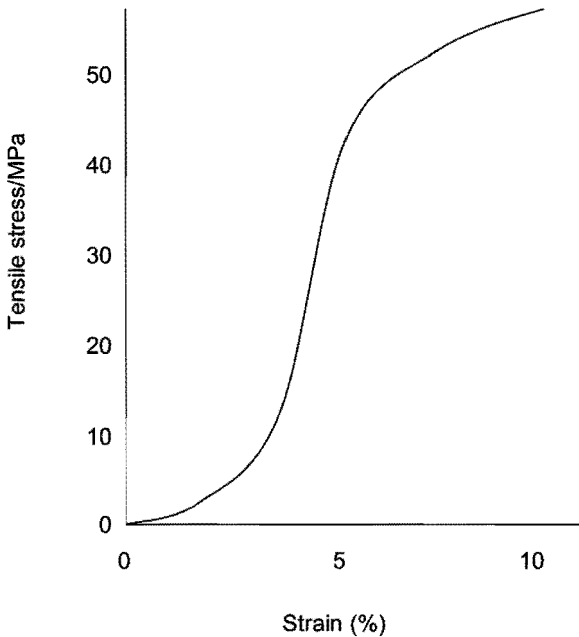


Figure 9.9. Deformation behaviour of tendon.

During slow stretching (2–10%/min, not very realistic) there is a curved part in the beginning of the graph, which is caused by the unfolding of the crimps in the tendon. Normally (strain rates of 20%/min) this is absent. The straight part of the graph is due to the stretching of the chains.

The tensile strength can vary between 20 and 140 MPa, but most fibres have a strength of 50–100 MPa.

9.3.3 Hard tissues

In general, these are a composite of proteins and ceramics. In humans, the ceramic material is usually a variation of calcium phosphate (bone). Elsewhere in nature, calcium carbonate and silica are also found.

Nacre

Nacre is not a human tissue, of course, but it is a very well studied example from shells. It consists mainly of small blocks of CaCO_3 with an organic protein–polysaccharide matrix in between (1–4 mass%). The matrix is layered: it has an acidic protein for attachment to the ceramic, a silk-like protein, and a polysaccharide (chitin), as shown in Figure 9.10.

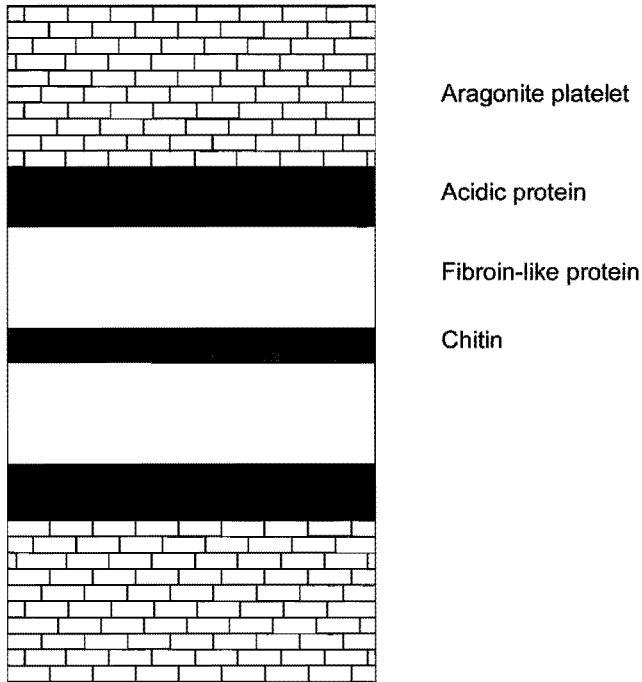


Figure 9.10. Layered structure of nacre.

Nacre can be deformed elastically up to 1% strain with a modulus that varies between $E = 60$ GPa (wet) and 70 GPa (dry). The mineral has a modulus of ca. 100 GPa, and the matrix has $E = 3$ GPa. The models we have introduced earlier for composites then give: $E = 95$ GPa (Voigt) or 39 GPa (Reuss). We see that the experimental modulus is indeed between the two extremes from the models.

For strains larger than 1% we get plastic deformation. Fracture only occurs at a strain of 20–30% (dry) or even 45–55% (wet). The necessary stress is 130 MPa during stretching, and 380 MPa during compression. So, the composite is very tough: the work of fracture is 400 J/m^2 (dry) and 600–1200 J/m^2 (wet).

This can be explained when we look at the structure: the layers of nacre are parallel to the shell surface, and contain small crystals of aragonite (0.3–0.5 μm thick). Aragonite has a modulus $E = 137$ GPa and a surface energy $\gamma = 0.23$ J/m^2 , which leads to a fracture toughness $K_{1C} = 0.25$ $\text{MPa}\cdot\text{m}^{1/2}$. The tensile strength of aragonite is 50–100 MPa, so there is a critical crack length of 2–8 μm . Such a crack can not fit inside the small crystals, so fracture can only occur in the matrix.

The aragonite blocks are shifted with respect to each other, so a crack can not grow straight ahead through the matrix, but must continuously switch its path, which

costs a lot of energy (see Figure 9.11). This can be compared to the way in which bricks and mortar are combined to a wall: here we also shift the bricks relative to each other to get a strong wall.

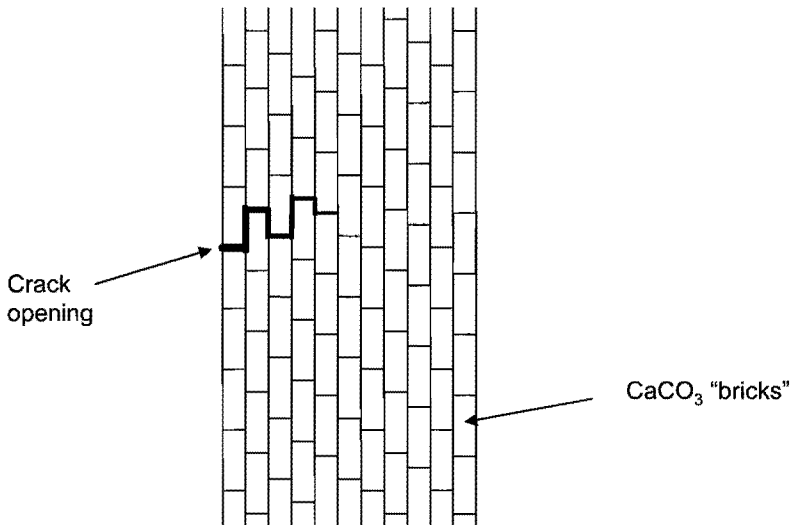


Figure 9.11. A fracture in nacre has to grow in changing directions between the crystallites.

Bone

Bone is a very complex material: not only is it a composite, but it is also built up in a hierarchical fashion, and contains blood vessels and cells. For this latter reason, bone is a very porous material: there can be a volume fraction of 20–30% consisting of holes. This is of course bad for the strength. Further, as is typical for most biological materials, bone is built up during growth, and can be repaired after fracture.

As a composite, bone consists mainly of collagen as protein and hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) as ceramic, and also other proteins, glycoproteins (covalently bound proteins and sugars), and protein–polysaccharide complexes.

On the smallest length scale ($0.1 \mu\text{m}$), bone is a “simple” composite of collagen fibres in a ceramic matrix. Ca. 1/3 of the dry mass of bone is collagen, and its parallel fibres direct the formation of the ceramic crystals. The matrix consists of small (ca. 4 nm thick, $50 \times 30 \text{ nm}$) crystals of hydroxyapatite. In young bone, there is also amorphous mineral present.

On a higher level ($10 \mu\text{m}$ -scale) there are two types of bone:

- **Woven bone**, with a random orientation of the collagen fibres, more mineral, and more amorphous mineral. This is the type of bone that is formed first during growth or repair.
- **Lamellar bone**, with fibres in $5 \mu\text{m}$ thick lamellae that run in the length direction of the bone. This form is the most common one.

On even higher length scales these forms lead to two main types of bone:

- **Laminar bone**, alternating layers of woven and lamellar bone.
- **Haversian bone**, which is built up from cylindrical building blocks: the **osteons** ($200 \mu\text{m}$ diameter, see Figure 9.12).

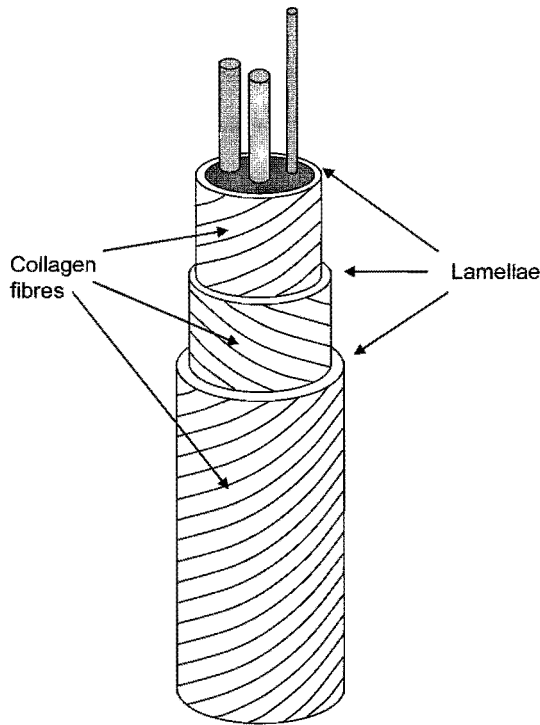


Figure 9.12. Structure of the osteon, with arteries, veins and nerves in the central channel.

The fibre orientation in the osteons is very important for the final properties of the bone, and it is therefore optimized for the function of the bone.

These types can now form the most common bone structures:

- **Compact bone** (or cortical bone), which is best suited for bending and twisting forces.
- **Cancellous bone** (also called spongy or trabecular bone), which occurs in places where compression forces are felt. This is built up from small bone columns (trabeculae), and is very porous. It usually is covered with a layer of compact bone. The orientation of the trabeculae is optimized to carry the stress with the minimum amount of material.
- **Flat bone**, a sandwich of spongy bone between two compact bone layers.

Bone is a visco-elastic material, so there will be a dependence on the speed of the measurements. During a rapid measurement there is an elastic deformation up to a strain of 1%, and after that there is yield. Fracture occurs at a strain of 4%. There is no necking: bone shows brittle fracture.

Bone is also anisotropic: it is strongest in the length direction. The Poisson ratio of bone can vary between 0.13 and 0.30.

Haversian bone in humans typically has a modulus of 17 GPa during stretching, and 19 GPa in compression. The tensile strength is 220 MPa during compression.

For the various types of bone, we find elastic moduli between 5 and 30 GPa. The matrix (hydroxyapatite) has a modulus $E = 130$ GPa, and a tensile strength of 100 MPa at a strain of 0.1%. The collagen fibres have $E = 1$ GPa, and a tensile strength

of 50 MPa. The models we have derived earlier for composites now predict a range for the modulus of 2.5 to 50 GPa, which is indeed correct for bone. Of course this depends on the amount of ceramic matrix (or ash content), as seen in Figure 9.13. The amount of ceramic matrix is also important for other mechanical properties of bone. The bending strength e.g. varies between 30 and 300 MPa, depending on the amount of ceramic (50–70%).

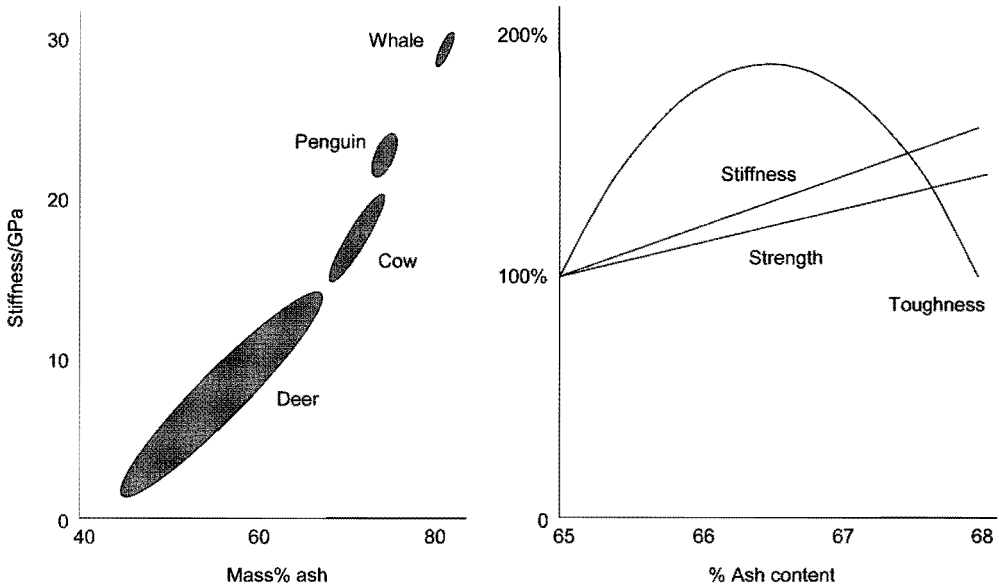


Figure 9.13. Left: The amount of ceramic ("ash") determines the stiffness of bone. Right: Other properties of bone are also dependent on the amount of ceramic.

Tooth

Tooth is built up from various components, but for the mechanical properties mostly **enamel** and **dentine** are important.

The enamel on the exterior of the tooth is 95% ceramic, but the inner dentine is 70% ceramic and 20% biopolymer (and 10% water). Because of this, dentine is more flexible, but also more sensitive to infections (caries) when the enamel layer is broken.

Dentine is quite similar to bone: there is a matrix of small crystals ($2 \times 50 \times 25$ nm) in a matrix of polysaccharides and collagen. However, here there are tubules in the matrix with a strongly mineralized wall.

Tooth is mainly stressed in compression (up to 20 MPa), and that many times a day. Dentine has a Young's modulus of 12 GPa, and a compressive strength of 200 MPa. The work of fracture varies from 270 J/m^2 (perpendicular to the tubules) to 550 J/m^2 (parallel to the tubules).

Enamel mainly consists of ceramic material in the form of prisms. It is much more rigid ($E = 40\text{--}80$ GPa) and equally strong as dentine (compressive strength 200–330 MPa). The work of fracture varies from 13 J/m^2 (parallel to the prisms) to 200 J/m^2 (perpendicular to the prisms).

Intermezzo

Enamel will dissolve at $\text{pH} < 5.5$, and then the dentine is attacked by bacteria and broken down. The usual solution is to drill away the dentine, and fill it with amalgam or a polymer. The drilling may now be over, since the weakened dentine can be selectively dissolved by a chemical treatment at very high pH (ca. 11), where the enamel does not dissolve. After that, the hole can be filled as usual.

Problems

9.1. A composite consists of 40 vol% continuous E-glass fibres in an epoxy matrix. The elastic modulus of the glass and epoxy are 76 and 2.7 GPa.

- Calculate the composite modulus parallel to the fibre axis.
- What is the composite modulus perpendicular to the fibre axis?

9.2. It is desired that the fibres support 90% of the load in a composite containing aligned, continuous high-modulus carbon fibres embedded in an epoxy matrix. What volume fraction of fibre will be required?

For epoxy assume $\rho = 1.3 \text{ Mg/m}^3$ and $E = 3 \text{ GPa}$.

9.3. The Young's modulus for a composite containing 60 vol% continuous aligned fibre is 44.5 GPa when tested along the fibre axis, but only 7.4 GPa when tested normal to the fibre axis. Determine the Young's modulus for the fibre and for the matrix.

9.4. A composite containing 25 vol% aligned continuous carbon fibres in an epoxy matrix fails at a tensile stress of 700 MPa. If the fibre tensile strength is 2.7 GPa, what is then the matrix yield strength?

9.5. In an aligned fibreglass composite the tensile strength of the 10- μm diameter E-glass fibres is 2.5 GPa, the matrix has a modulus of 2.3 GPa and a yield strength of 6 MPa, and the interfacial shear strength is 0.1 GPa.

- What is the optimal cut fibre length?
- If chopped glass fibre of optimal length is used, what volume fraction should be added to the matrix to produce a composite tensile strength of 1 GPa?
- What is the work of fracture for the composite in b.?
- Calculate the Young's modulus for the composite in b., assuming that the force is in the direction of the fibres.
- Calculate the fracture toughness for the composite in b., and compare this to the toughness of the matrix (ca. $0.5 \text{ MPa}\cdot\text{m}^{1/2}$).

9.6. A piece of dog skin (20 mm long, 4 mm wide and 3 mm thick) is used in a tensile test. The force increases first from 0 to 5 N, up to a strain of 20%. After that, the force rises to 130 N at 50% strain, where the skin breaks.

- Calculate the tensile strength of this skin.
- Calculate the Young's moduli for the first and second regions of the test (assume linear graphs).
- Explain the presence of two regions in terms of molecules.
- Calculate the toughness of this skin.

9.7.* We wish to make an enamel-like composite for a tooth prosthesis with quartz ($E = 60$ GPa, $\sigma_T = 48$ MPa) and Kevlar fibres (12 μm diameter).

- a. What volume fraction fibres is necessary to get the same modulus as enamel (80 GPa)? Explain which model(s) you use.

For the desired tensile strength of the composite, it is found that the optimal length of the fibres is 1 mm.

- b. Calculate the interfacial shear stress between quartz and Kevlar. Do you expect a strong interaction between quartz (SiO_2) and Kevlar (a polyamide)?
- c. Why don't we use quartz for the enamel replacement? It has about the right modulus.

Appendices

Education is an admirable thing, but it is well to remember from time to time that nothing worth knowing can be taught.

Oscar Wilde
(1854–1900)

Appendix A

English–Dutch glossary; List of symbols

If the Dutch word is different, it is included in parentheses.

If there is a symbol for the quantity, it is included after the description in parentheses.

- **adhesion** (adhesie): attraction between two different compounds (W_a [J/m^2])
- **anisotropic** (anisotroop): different value in different directions
- **annealing** (temperen, herstelgloeien): keeping a material at a high temperature to change its properties
- **atactic** (atactisch): random stereochemistry in a **polymer** chain
- **austenite** (austeniet): iron–carbon **phase** with **FCC** structure (γ -Fe)
- **bainite** (bainiet): **microstructure** of **ferrite** and **cementite** with coarse **grains**
- **BCC**: **body-centred cubic lattice** in a **crystal**
- **binary phase diagram** (binair fasendiagram): **phase diagram** with two **components**
- **bioceramic** (biokeramiek): **ceramic** compound occurring in a living system
- **biological material** (biologisch materiaal): material originating from a living system
- **biomaterial** (biomateriaal): material inserted in a living system
- **biomineralization** (biomineralisatie): formation of **crystals** in a living system
- **biopolymer** (biopolymeer): **polymer** originating from a living system
- **body-centred cubic** (ruimtelijk gecentreerd kubisch): kind of **crystal** structure
- **Bravais lattice** (Bravais rooster): one of 14 possible **crystal** structures
- **brittle** (bros): having a low **toughness** and high σ_Y ; absorbs little energy before breaking
- **brittle fracture** (brosse breuk): fracture due to rapid **crack** growth in **ceramics** and **metals**
- **bulk**: average, usually the same as interior; the surface is different
- **bulk composition** (bulksamenstelling): average composition; the **surface composition** is different
- **cancellous bone** (spongieus of trabeculair bot): very porous form of bone
- **cartilage** (kraakbeen): biological **composite** based on **collagen fibres** and a strongly hydrated matrix inside the **fibre** network
- **cast iron** (gietijzer): Fe/C mixture with more than 2.14 wt% C
- **CCT-diagram**: continuous–cooling–transformation diagram; shows how the **phases** of a material change during cooling as a function of time
- **cellular material** (cellulair materiaal): material built up as holes and walls
- **cellulose**: plant **polysaccharide**
- **cementite** (cementiet): Fe_3C **ceramic** in Fe/C mixtures
- **ceramic** (keramiek): material built up with **covalent**, **network** or **ionic bonds**
- **close-packed structure** (dichtstgepakte structuur): **crystal** structure with the maximum filling of space by atoms
- **cohesion** (cohesie): attraction between two surfaces of the same material (W_c [J/m^2])
- **coil** (kluwen): irregularly folded shape adopted by long **macromolecules**
- **cold working** (koud bewerken): processing technique where the material is deformed at low temperature
- **collagen** (collageen): protein that functions as **fibre** in biological **composites**
- **compact bone** (compact of corticaal bot): bone with a low porosity
- **component**: one of the constituents of the mixtures in a **phase diagram**

- **composite** (composiet): material built up from two or more different simple or **monolithic materials**
- **compression** (samenpersen): reducing the length in the direction of the force
- **connective tissue** (bindweefsel): biological **composite** built up from **collagen fibres** in a **visco-elastic** matrix
- **contact angle** (contacthoek): angle that a liquid drop makes with a surface; indicative for **surface tensions**
- **copolymer** (copolymeer): **polymer** built up from two or more different monomers
- **covalent bond** (covalente binding): strong chemical bond based on orbital overlap
- **covalent network** (covalent netwerk): material where all atoms are connected by **covalent bonds**
- **crack** (breuk): small imperfection in a material that can lead to complete fracture
- **creep** (kruip): increasing **strain** during constant **stress**
- **critical crack length** (kritische breuklengte): minimum length necessary for a **crack** before it can grow according to Griffith's theory (c^* [m])
- **critical shear stress** (kritische zwichtspanning): **shear stress** where layers of atoms start sliding over each other in a specific **slip system** (τ_c [Pa])
- **critical stress** (kritische spanning): minimum **stress** necessary for a crack to start growing according to Griffith's theory (σ^* [Pa])
- **crosslink** (vernetting): strong bond (usually covalent) between two macromolecules
- **crystal** (kristal): material with a very regular position for the atoms or molecules
- **crystalline** (kristallijn): material built up as **crystals**
- **crystal system** (kristalstelsel): specific type of **crystal** structure, based on its symmetry; there are 7 systems
- **CsCl-structure** (CsCl-structuur): kind of **crystal** structure
- **cubic structure** (kubische structuur): type of **crystal** structure with cubic **unit cells**
- **defect** (fout): irregularity in a **crystal lattice**
- **deformation angle** (vervormingshoek, afschuifhoek): measure of deformation during **shear** (γ [rad])
- **degree of freedom** (vrijheidsgraad): parameter (usually pressure, temperature, and chemical composition) that can be changed freely within one region of a **phase diagram**
- **degree of polymerization** (polymerisatiegraad): number of monomers that form a macromolecule; the "length" of the polymer chain (DP [-])
- **dentine**: biological composite in the interior of teeth
- **dermis** (leerhuid): layer of skin that determines its mechanical properties
- **dewetting** (druppelvorming): formation of droplets of a liquid on a surface
- **diamond cubic structure** (diamantstructuur): kind of **crystal** structure
- **dipole-dipole interaction** (dipool-dipool interactie): weak bond between **molecules** based on the electrostatic attraction between dipoles
- **dislocation** (dislocatie): linear **defect** in a **crystal lattice**
- **dispersion hardening** (dispersieharding): increasing the strength of a material with large particles of another material
- **ductile** (week): low **yield strength**
- **ductile fracture** (taaie breuk): fracture due to **plastic deformation** and **necking** in **metals**
- **ductility** (vervormbaarheid): measure for the permanent deformation of a material after fracture; also a measure for **toughness**
- **edge dislocation** (randdislocatie): **dislocation** in a **crystal** along a line, where the defect is perpendicular to the line

- **elastic component of modulus** (opslagmodulus): for **visco-elastic** materials, this determines the elastic part of the behaviour (E' [Pa])
- **elastic deformation** (elastische vervorming): **reversible deformation** of a material, usually involving only the **stretching** or **compression** of bonds
- **elastin** (elastine): protein with typical **rubber** properties
- **elastomer** (elastomeer): **rubber**, polymeric material with a small number of **crosslinks**
- **electrostatic bond** (elektrostatistische binding): strong bond between **ions** based on Coulombic attraction
- **elongation factor** (rekfactor): dimensionless measure for the change in length of a material (λ [-])
- **enamel** (glazuur): outer layer of teeth; biological **composite** based mainly on hydroxyapatite
- **engineering strain** ("normale" rek): **strain** calculated with respect to the original length of the material (ε [-])
- **engineering stress** ("normale" spanning): **stress** calculated with respect to the original cross section of the material (σ [Pa])
- **entanglements** (verknoppingen): places where long **macromolecules** are intertwined with each other, which hinders movements
- **entropy** (entropie): measure for the number of possibilities a system has to distribute its energy (S [J/K])
- **epidermis** (opperhuid): dead outer layer of skin, mostly consisting of **keratin**
- **eutectic** (eutecticum): region in a **phase diagram** where three **phases** exist simultaneously
- **face-centred cubic** (vlakgecentreerd kubisch): kind of **crystal** structure
- **FCC: face-centred cubic lattice** in a **crystal**
- **ferrite** (ferriet): Fe/C **phase** with a **BCC** structure (α -Fe)
- **fibre** (vezel): material in a shape with a length far larger than its diameter; can be built up from oriented **macromolecules**
- **flat bone** (plat bot): type of bone that is a sandwich of **cancellous bone** between two layers of **compact bone**
- **flexible** (slap): low **Young's modulus**
- **flexural stiffness** (buigingsstijfheid): modulus for **elastic deformation** during bending
- **fracture toughness** (breuktaaiheid, scheurweerstand): measure for the resistance of a material against **crack** growth
- **free volume** (vrij volume): difference in volume between glassy **polymer** and undercooled molten **polymer**
- **GAG: glycosaminoglycan**
- **gel**: solution with a very high viscosity, e.g. due to dissolved **macromolecules**
- **glass** (glas): material with strong **covalent** or **ionic bonds**, but without order; also: **thermoplast** or **elastomer** below T_g
- **glass (transition) temperature** (glas(overgangs)temperatuur): temperature where the **glass transition** occurs; dependent on the speed of measurement (T_g [K])
- **glass transition** (glasovergang): process where a material changes from a **glass** to a liquid
- **glycosaminoglycan: polysaccharides** with charged groups
- **grain** (korrel): a **single-crystal** region in a **polycrystalline** material
- **grain boundary** (korrelgrens): boundary between different **grains** in a **polycrystalline** material

- **hardness** (hardheid): empirical material property
- **Haversian bone**: type of **compact bone** built up from **osteons**
- **HCP**: **hexagonal close packed lattice** in a **crystal**
- **hexagonal structure** (hexagonale structuur): type of **crystal** structure with hexagonal **unit cells**
- **hexagonal close packed structure** (hexagonale dichtstgepakte structuur): kind of **crystal** structure
- **hierarchical material** (hiërarchisch materiaal): material built up differently on different length scales
- **Hooke's law** (wet van Hooke): linear relation between **stress** and **strain**
- **hydrogen bond** (waterstofbrug): weak bond between **molecules** based on **dipole-dipole interaction** when N–H, O–H, or F–H groups are present
- **hysteresis** (hysterese): occurs when a process does not follow the same route on reversal; usually leads to the loss of energy as heat
- **internal friction** (interne wrijving): loss of energy during deformation due to movements of **macromolecules** along each other
- **ion**: electrically charged atom or **molecule**
- **isostrain model**: also known as **Voigt model**; describes the **stiffness** of materials in parallel
- **isostress model**: also known as **Reuss model**; describes the **stiffness** of materials in series
- **isotactic** (isotactisch): **macromolecule** with the same stereochemistry in each repeating unit
- **isotropic** (isotroop): the same value in all directions
- **keratin** (keratine): **hierarchical protein** material built up from α -helices
- **lamellar** (lamellair): built up in layers
- **lamellar bone**: form of bone built up from small lamellae
- **laminar** (laminair): built up in layers
- **laminar bone**: form of bone built up from alternating layers of **woven** and **lamellar bone**
- **lamp brush** (flessenborstel): model for the structure of the **composite** soft tissues
- **lattice** (rooster): regular distribution of **lattice points** in space
- **lattice parameter** (roosterconstante): length of the sides of the **unit cell** (a or c [m])
- **lattice point** (roosterpunt): mathematical point in a **lattice** where one or more atoms can be located
- **lever rule** (hefboomregel): rule that determines how much of the two **phases** is formed in a two-phase region of a **phase diagram**
- **line defect** (lijnvormige fout): **defect** that forms a line in a **crystal lattice**
- **liquidus**: line in a **phase diagram** that indicates the composition of a liquid **phase** in a two-phase region
- **loss component of modulus** (verliesmodulus): for **visco-elastic** materials, this determines the viscous part of the behaviour (E'' [Pa])
- **martensite** (martensiet): **microstructure** of **steel** that is formed during very quick cooling
- **macromolecule** (macromolecuul): large **molecule** built up from repeating monomer units; basic structure of **polymers**
- **macroscale** (macroschaal): length scale in the range of practical materials (> 1 mm)
- **maximum strain** (breukrek): strain at which fracture occurs (ϵ_{\max} [–])

- **mechanical properties** (mechanische eigenschappen): properties of a material that determine its behaviour under **stress**
- **melting temperature** (smelt-temperatuur): temperature where a solid changes into a liquid (T_m [K])
- **mesoscale** (mesoschaal): length scale in the range of typical defects (10 nm–0.1 mm)
- **metal** (metaal): material built up from atoms that are kept together by a **metallic bond**
- **metallic bond** (metaalbinding): strong chemical bond where the atoms share their valence electrons in a common “electron sea”, a molecular orbital that spans the entire material
- **microscale** (microschaal): length scale in the range of atoms and bonds (0.1–1 nm)
- **microstructure** (microstructuur, textuur): structure of **grains** in a **polycrystalline** material
- **Miller indices**: numbers that indicate directions or planes in a **crystal lattice**
- **molecule** (molecuul): set of atoms kept together by **covalent bonds**
- **monolithic material** (monolithisch materiaal): material built up from a single compound; has the same chemical composition everywhere in the **bulk**
- **morphology** (morfologie, textuur): **microstructure** of a material
- **nacre** (paarlemoer): biological **composite** in shells
- **necking** (insnoering): sudden reduction in cross-sectional area of a material after **yield** and **plastic deformation**
- **network** (netwerk): **molecules** or atoms that are connected with multiple **covalent bonds**
- **number-averaged molar mass** (aantalgemiddelde molmassa): average molar mass of a **polymer** mixture, based on mole fractions (M_n [kg/mol])
- **osteon**: basic cylindrical structure of **Haversian bone**
- **particulate** (deeltjesversterkt): used for a **composite** material with particles in a matrix
- **pearlite** (perliet): **microstructure** of **steel** with fine layers of **ferrite** and **cementite**
- **phase** (fase): region in a material with a specific chemical composition and/or aggregation state
- **phase angle** (fasehoek): measure for the difference between the behaviour of **stress** and **strain** in the cyclic deformation of a **visco-elastic** material
- **phase diagram** (fasendiagram): diagram that indicates what **phases** a material adopts as a function of e.g. temperature and chemical composition
- **phase rule** (fasenregel): rule that determines how many **degrees of freedom** are available for a system with a certain number of **phases**
- **planar defect** (oppervlaktefout): **defect** in a **crystal** structure along a plane, e.g. a **grain boundary**
- **plastic deformation** (plastische vervorming): irreversible deformation, where the bonds between atoms or **molecules** are broken, and reformed between other atoms or **molecules**
- **plasticizer** (weekmaker): small molecule that is added to a **polymer** material to change its **mechanical properties**; usually softens the material
- **point defect** (puntdefect): **defect** in a **crystal** structure on one site, e.g. a vacancy
- **Poisson ratio** (constante van Poisson): dimensionless measure for the change in cross-sectional area during **stretching** or **compression** (ν [-])
- **polycondensation** (polycondensatie): reactions to synthesize **macromolecules** that involve release of water (formation of esters, amides, etc.)

- **polycrystalline** (polykristallijn): material built up from different **single-crystal grains** that stick together
- **polydispersity** (polydispersiteit): measure for the spread in molar masses in a mixture of **macromolecules** (D [-])
- **polymer** (polymeer): material built up from **macromolecules**
- **polymerization** (polymerisatie): chemical reactions that couple monomers to form a **macromolecule**
- **polymorphic** (polymorf): having more than one **crystal** structure, depending on the circumstances during crystallization
- **polysaccharide**: **polymer** of sugar monomers
- **PPL**: **protein** core with **polysaccharides** attached; building block of the **cartilage** matrix
- **precipitation hardening** (precipitatieharding): strengthening a material by inserting small **crystals** of another material
- **protein** (eiwit): **polymer** of amino acids
- **protein-polysaccharide complex** (eiwit-polysaccharide complex): complex between **proteins** and **polysaccharides** without **covalent bonds**
- **proteoglycan**: combination of **protein** and **GAG**, linked by **covalent bonds**
- **radical polymerization** (radicaalpolymerisatie): reactions to synthesize **macromolecules** that involve radicals
- **radius of gyration** (gyratiestraal): measure for the size of a random coil (R_g [m])
- **random-coil model** (kluwenmodel): model to describe the behaviour of a **macromolecule** without a regular structure
- **recovery** (herstel): after **plastic deformation**, there will often be a small elastic part of the deformation that shortens the material after the force is removed
- **resilience** (veerkracht): energy that can be absorbed reversibly (E_{el} [J/m³])
- **resin** (hars): common name for **thermo-harders**
- **Reuss model**: describes the **stiffness** of materials in series
- **rock salt structure** (steenzoutstructuur): kind of **crystal** structure
- **root-mean-square value** (gemiddelde van de som van de kwadraten): way to average random values
- **rubber**: **elastomer**, **polymer** with a small number of **crosslinks**
- **salt** (zout): material built up from **ions** and kept together by **electrostatic bonds**; all inorganic salts are **ceramics**
- **SC**: **simple cubic lattice** in a **crystal**
- **screw dislocation** (schroefdislocatie): **dislocation** in a **crystal** along a line, where the defect is parallel to the line
- **shear modulus** (glijmodulus): material property that indicates the **stiffness** during **shearing** (G [Pa])
- **shear stress** (afschuifspanning): stress that runs parallel to a surface (τ [Pa])
- **shearing** (afschuiven): deforming a material with a force parallel to a surface
- **silk** (zijde): strong **protein**, used by spiders as construction material
- **simple cubic** (simpel kubisch): kind of **crystal** structure
- **single crystal** (éénkristal): material built up from one **grain**; one **crystal lattice** spans the entire material
- **slip system** (glijstelsysteem): a plane and a direction in a **crystal** structure which define the movement of layers of atoms
- **solid solution** (vaste oplossing): presence of isolated strange atoms in another solid

- **solidus**: line in a **phase diagram** that indicates the composition of a solid **phase** in a two-phase region
- **spherulite** (sferuliet): **spherical structure found in polymers** built up from crystalline lamellae and amorphous regions
- **spreading coefficient** (spreidingscoëfficiënt): property that determines whether a liquid will form a film on a surface
- **steel** (staal): Fe/C mixture with less than 2.14 wt% C
- **stiff** (stijf): high **Young's modulus**
- **stiffness** (stijfheid): measure for the **force** necessary to reach a certain **elongation** during **elastic deformation** of a piece of material; related to the **Young's modulus** of the material
- **storage component of modulus** (opslagmodulus): for **visco-elastic** materials, this determines the elastic part of the behaviour (E' [Pa])
- **strain** (rek): dimensionless measure for the change of the length of a material (ε [-])
- **strain hardening** (koudeverharding): increasing resistance against **yield** after stretching a material and testing it again
- **stress** (spanning): force per unit area (σ [Pa])
- **stress concentration** (spanningsconcentratie): at the tip of a **crack**, a larger **stress** is found than applied from the outside
- **stress intensity** (spanningsintensiteit): combined measure for both the **stress** and **crack** length in a material (K [$\text{Pa} \cdot \text{m}^{1/2}$])
- **stress relaxation** (spanningsrelaxatie): decreasing **stress** at constant **strain**
- **strong** (sterk): usually indicates high **tensile strength**, but may also mean high **yield strength**
- **surface composition** (oppervlakte-samenstelling): chemical composition of the surface, as opposed to the **bulk composition**
- **surface tension** (oppervlaktetensie): excess energy on a surface due to the missing bonds (γ [J/m^2] or [N/m])
- **syndiotactic** (syndiotactisch): **macromolecule** with alternating stereochemistry in each repeating unit
- **tensile strength** (treksterkte): maximum **engineering stress** that can be carried by a material (σ_T [Pa])
- **tension** (uitrekken): increasing the length of a material in the direction of the force
- **thermo-harder**: **polymer** that forms a **covalent network** after processing, and then can not be processed again
- **thermoplast**: **polymer** that is built up from **macromolecules** without **crosslinks**; can be molten and processed repeatedly
- **tie line** (conode): constant-temperature line in a two-phase region of a **phase diagram** that indicates the compositions of the two related **phases**
- **tough** (taai): absorbs a lot of energy before fracture; high **toughness**
- **toughness** (taaiheid): area under **stress-strain curve** ($[\text{J}/\text{m}^3]$), or **fracture toughness** (K_{1C} [$\text{Pa} \cdot \text{m}^{1/2}$]); also reflected in **ductility**
- **true strain** (ware rek): **strain** calculated at each moment with respect to the immediately preceding length of a material (ε_t [-])
- **true stress** (ware spanning): **stress** as defined by the actual cross-sectional area during deformation (σ_t [Pa])
- **TTT-diagram**: diagram that indicates how the Transformation of a material is influenced by Time and Temperature
- **unit cell** (eenheidscel): repeating unit in a **crystal lattice**

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- **van der Waals attraction** (van der Waals attractie): very weak bond between **molecules** based on induced dipoles
 - **visco-elastic** (visco-elastisch): mechanical behaviour is time-dependent, and determined by both **elastic deformation** and **plastic deformation** (viscous flow)
 - **Voigt model**: describes the **stiffness** of materials in parallel
 - **weak** (zwak): usually indicates low **tensile strength**; may also mean low **yield strength**
 - **weight-averaged molar mass** (gewichtsgemiddelde molmassa): average molar mass of a **polymer** mixture, based on mass fractions (M_w [kg/mol])
 - **wetting** (bevochtigen): formation of a film of a liquid on a surface
 - **whisker** (haartje): very thin and long **single crystal**
 - **work hardening** (koudeharding): increasing the strength of a material by **cold working**
 - **work of fracture** (breukenergie): energy necessary for **crack** growth (W_f [J/m²])
 - **woven bone** (plexiform bot): form of bone with random orientation of the **collagen fibres** and some amorphous mineral
 - **yield** (vloei, zwichten): beginning of **plastic deformation** after **elastic deformation**
 - **yield strain** (rekgrens): **strain** where **yield** begins (ϵ_Y [-])
 - **yield strength** (zwichtsterkte): **stress** where **yield** begins as material property (σ_Y [Pa])
 - **yield stress** (zwichtspanning): **stress** where **yield** begins (σ_Y [Pa])
 - **Young's modulus**: material property that indicates the **stiffness** during **elastic deformation** (E [Pa])
 - **zinc blende structure** (zinkblende of sfaleriet-structuur): kind of **crystal** structure

List of symbols

Roman

A [m^2]	area
A [J/m^m]	constant for attraction between atoms
A' [m^2]	area of tilted cross section
A_0 [m^2]	original area
\mathcal{A} [-]	intercept of x-axis in unit cell
a [m]	length of unit cell side
a [-]	parameter for line or plane in unit cell
B [J/m^n]	constant for repulsion between atoms
\mathcal{B} [-]	intercept of y-axis in unit cell
b [m]	length of unit cell side
b [-]	parameter for line or plane in unit cell
C [-]	number of components in phase diagram
C_f [$Pa \cdot kg/mol$]	constant in relation of σ_T vs. M_n
C_g [$Pa \cdot m^{1/2}$]	constant in relation of σ_Y vs. d_g
C_r [-]	correction factor for $\langle r_c^2 \rangle$
C_T [$K \cdot kg/mol$]	constant in relation of T_g vs. M_n
C [-]	intercept of z-axis in unit cell
c [m]	length of unit cell side
c [m]	crack length (surface) or half of crack length (internal)
c^* [m]	critical crack length in Griffith theory
c [-]	parameter for plane in unit cell
D [-]	polydispersity
DP [-]	degree of polymerization
d [m]	distance between planes in a crystal
d_f [m]	fibre diameter
d_g [m]	grain diameter
E [Pa]	Young's modulus
E' [Pa]	elastic or storage modulus
E'' [Pa]	loss modulus
E_{crack} [J/m]	energy of growing crack
E_{el} [J/m^3]	resilience
E_p [Pa]	Young's modulus due to primary (covalent) bonds
E_s [Pa]	Young's modulus due to secondary (weak) interactions
e [C]	charge of proton
F [N]	force
F' [N]	component of force
\mathcal{F} [-]	degrees of freedom in phase diagram
F_a [N]	force between atoms
f [-]	fraction of covalent contribution to E
f_i [-]	fraction (mole or weight) of phase i in total
G [Pa]	shear modulus
h [-]	Miller index
i [-]	Miller index
j [-]	number of repeating units in a macromolecule
K [$Pa \cdot m^{1/2}$]	stress intensity

K_{pl} [Pa]	constant of plastic deformation
K_{1C} [Pa·m ^{1/2}]	fracture toughness
k [-]	Miller index
k_s [N/m]	spring constant
L [m]	length
L_{opt} [m]	optimum length of fibre
L_s [m]	segment length in random-coil model
L_x [m]	length in x-direction
L_y [m]	length in y-direction
L_z [m]	length in z-direction
L_0 [m]	original length
M_j [kg/mol]	molar mass of macromolecule with j monomers
M_n [kg/mol]	number-averaged molar mass
M_w [kg/mol]	weight-averaged molar mass
M_0 [kg/mol]	molar mass of repeating unit
m [-]	exponent of attraction between atoms
N [mol]	total number of macromolecules
N_A [mol ⁻¹]	Avogadro's number: number of particles in a mole
N_j [mol]	number of macromolecules with DP = j
N [-]	strain hardening exponent in plastic deformation
n [-]	exponent of repulsion between atoms
n_s [-]	number of segments in random-coil model
P [-]	number of phases
R [m]	interatomic distance
R_0 [m]	equilibrium interatomic distance
R_1 [m]	parameter in Orowan model
R_g [m]	radius of gyration
r [m]	radius of atom
r_c [m]	distance between chain ends
r_+ [m]	radius of cation
r_- [m]	radius of anion
$\langle r_c^2 \rangle$ [m ²]	root mean square of r_c
S [J/K]	entropy
S_{ji} [J/m ²]	spreading coefficient of j on i
T [K]	temperature
T_g [K]	glass transition temperature
$T_{g,\infty}$ [K]	T_g at infinite molar mass
T_m [K]	melting temperature
t [s]	time
U [J]	energy of pair of atoms or ions
U_0 [J]	U at $R = R_0$
V [m ³]	volume
V_i [-]	volume fraction of substance i
V_0 [m ³]	original volume
$W_{a,ij}$ [J/m ²]	adhesion between substance i and j
$W_{c,i}$ [J/m ²]	cohesion of substance i
W_f [J/m ²]	work of fracture
w [J/m ³]	absorbed energy per cycle
w_j [-]	mass fraction of macromolecules with DP = j
x [-]	x-coordinate

x_c [m]	critical fibre length
x_i [-]	composition (mole or weight fraction) of phase i
x_j [-]	mole fraction of macromolecules with $DP = j$
x_0 [-]	average or initial composition of whole system (mole or weight fraction)
y [-]	y -coordinate
z [-]	z -coordinate
z_- [-]	charge of anion as a multiple of e
z_+ [-]	charge of cation as a multiple of e

Greek

α [rad]	angle in unit cell
α_s [rad]	angle in slip system
β [rad]	angle in unit cell
β_s [rad]	angle in slip system
γ [rad]	angle in unit cell
γ [rad]	deformation angle during shear
γ [J/m ²]	surface energy
γ_i [J/m ²]	surface energy of substance i versus air
γ_{ij} [J/m ²]	surface energy of interface between substance i and j
δ [rad]	phase angle
ε [-]	strain
ε_c [-]	constant strain during stress relaxation
ε_{max} [-]	maximum strain at breaking, or during dynamical testing
ε_t [-]	true strain
ε_x [-]	strain in x -direction
ε_Y [-]	yield strain
ε_y [-]	strain in y -direction
ε_z [-]	strain in z -direction
ε_0 [F/m]	dielectric constant of vacuum
η [Pa·s]	viscosity
θ [rad]	arbitrary angle
λ [-]	elongation
ν [-]	Poisson ratio
ν [Hz]	frequency
ρ [kg/m ³]	density
ρ_c [m]	radius of curvature at crack tip
σ [Pa]	tensile stress
σ_a [Pa]	externally applied stress
σ_c [Pa]	constant stress during creep
σ_{int} [Pa]	internal stress at crack tip
σ_{max} [Pa]	maximum stress in Orowan model, or during dynamical testing
σ_r [-]	characteristic radius of polymer coil
σ_T [Pa]	tensile strength
$\sigma_{T,\infty}$ [Pa]	tensile strength at infinite molar mass
σ_t [Pa]	true stress
σ_Y [Pa]	yield stress
$\sigma_{Y,sc}$ [Pa]	yield stress of single crystal
σ^* [Pa]	critical stress in Griffith model

τ [Pa]	shear stress
τ_C [Pa]	critical shear stress in single crystal
τ_{fm} [Pa]	interfacial shear strength for fibre and matrix
τ_K [s]	creep relaxation time for linear elastic solid (τ_σ in the 1 st edition)
τ_{max} [Pa]	theoretical maximum shear stress
τ_R [s]	stress relaxation time for linear elastic solid (τ_ϵ in the 1 st edition)
τ_r [s]	relaxation time in Maxwell and Voigt models
ϕ [rad]	angle between vectors
ω [rad/s]	angular frequency

Only in Appendices

A_g [m ²]	area of ground surface
b_s [m ⁻¹]	constant in random-coil model
C_S [J/K]	constant in entropy equation
\dot{E} [Pa]	slope of σ, ϵ -curve
E_{fract} [J]	energy for fracture in Orowan model
F_c [N]	centripetal force
F_g [N]	gravitational force
G [Nm ² kg ²]	gravitational constant
g [m/s ²]	gravitational acceleration at the Earth's surface
k_B [J/K]	Boltzmann constant
M_\oplus [kg]	mass of Earth
N_c [m ⁻³]	chain density
h [m]	height above surface
h_{max} [m]	maximum height of tower
h_s [m]	height of geostationary orbit
L [m]	length of cable
m [kg]	mass of satellite
N_c [-]	coordination number in ionic structures
Q [J]	heat
r [m]	radius of orbit
r_s [m]	radius of geostationary orbit
r_\oplus [m]	radius of Earth
t [°C]	temperature in degrees Celsius
t' [°F]	temperature in degrees Fahrenheit
U [J]	internal energy
W [J]	work
$W(r_c)$ [m ⁻¹]	distribution function related to chain end distance
$W(x,y,z)$ [m ⁻³]	distribution function related to position
ΔS_{ac} [J/K]	entropy of all chains
ΔS_{sc} [J/K·m ³]	entropy of single chain
ΔS_{tot} [J/K]	total entropy of rubber
σ_C [Pa]	compression strength of brick

Only in Intermezzos

A [-]	Madelung constant
C_L [J/K]	heat capacity during elongation
G_c [J/m ²]	critical strain energy release rate, or toughness
K [Pa]	bulk modulus
i [-]	Miller–Bravais index for planes in a hexagonal unit cell
n [-]	scaling number for Miller–Bravais indices
n [-]	integer number in X-ray diffraction
t [-]	Miller–Bravais index for directions in a hexagonal unit cell
u [-]	Miller–Bravais index for directions in a hexagonal unit cell
v [-]	Miller–Bravais index for directions in a hexagonal unit cell
w [-]	Miller–Bravais index for directions in a hexagonal unit cell
γ_c [J/m ²]	surface energy
γ_p [J/m ²]	energy necessary for plastic deformation during fracture
ϵ_V [-]	strain based on volume change
η_0 [Pa·s]	standard viscosity
λ [m]	wavelength of X-rays

Appendix B More on true stress and strain

The force on a material during a tensile test is: $F = \sigma_t A$

We will work with the true strain (ε_t) here.

The maximum force is reached when: $\frac{dF}{d\varepsilon_t} = 0 = A \frac{d\sigma_t}{d\varepsilon_t} + \sigma_t \frac{dA}{d\varepsilon_t}$

Now with constant volume ($V = AL$): $\frac{dV}{d\varepsilon_t} = 0 = A \frac{dL}{d\varepsilon_t} + L \frac{dA}{d\varepsilon_t}$

Therefore: $\frac{dA}{d\varepsilon_t} = -\left(\frac{A}{L}\right) \frac{dL}{d\varepsilon_t}$

Since $\varepsilon_t = \ln\left(\frac{L}{L_0}\right)$ we get: $\frac{d\varepsilon_t}{dL} = \frac{1}{L}$, and: $\frac{dL}{d\varepsilon_t} = L$

So: $\frac{dA}{d\varepsilon_t} = -A$, and therefore: $A = A_0 e^{-\varepsilon_t}$

Also: $\frac{dF}{d\varepsilon_t} = A \frac{d\sigma_t}{d\varepsilon_t} - \sigma_t A$

With $\sigma_t = K_{pl} \varepsilon_t^N$, it then follows that: $\frac{dF}{d\varepsilon_t} = A(K_{pl} N \varepsilon_t^{N-1} - K_{pl} \varepsilon_t^N) = K_{pl} A \varepsilon_t^{N-1} (N - \varepsilon_t)$

The maximum force is found when $\frac{dF}{d\varepsilon_t} = 0$, which means:

$$\varepsilon_t = N$$

This is where necking occurs.

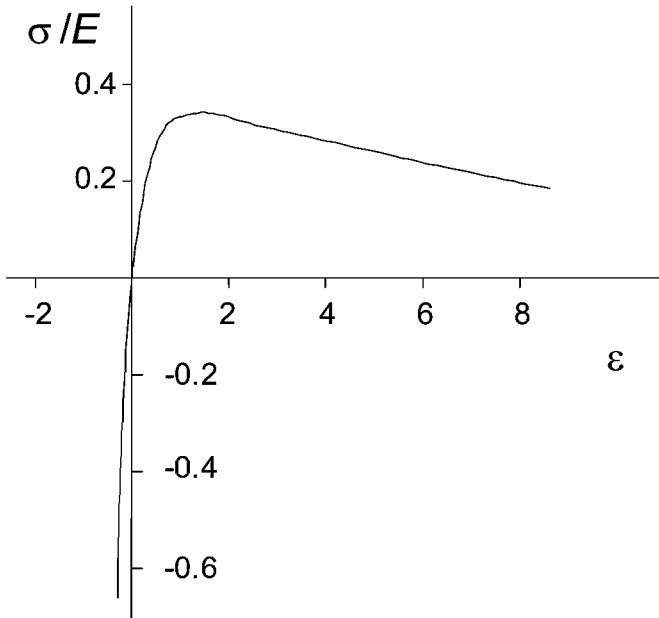
Before necking $\varepsilon_t < N$, so $\frac{dF}{d\varepsilon_t} > 0$: true stress increases faster than A decreases, so the material can carry a larger force F , or engineering stress $\sigma = F/A_0$.

After necking $\varepsilon_t > N$, so $\frac{dF}{d\varepsilon_t} < 0$: A decreases faster than true stress increases, so the material can carry a smaller force or engineering stress.

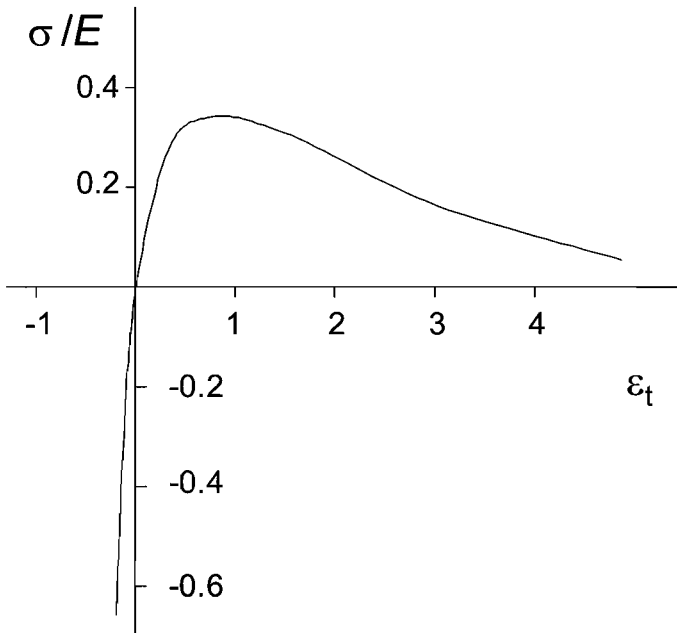
We will now look at an ideal elastic material, which has a linear relation between true stress and true strain: $\sigma_t = E\varepsilon_t$

It then follows from the relations above: $\frac{\sigma}{E} = \frac{\ln(1+\varepsilon)}{1+\varepsilon}$

When we plot $\frac{\sigma}{E}$ vs. ε , this automatically gives a maximum in σ during tension, because the cross-sectional area decreases faster than the force increases. This does not happen during compression.



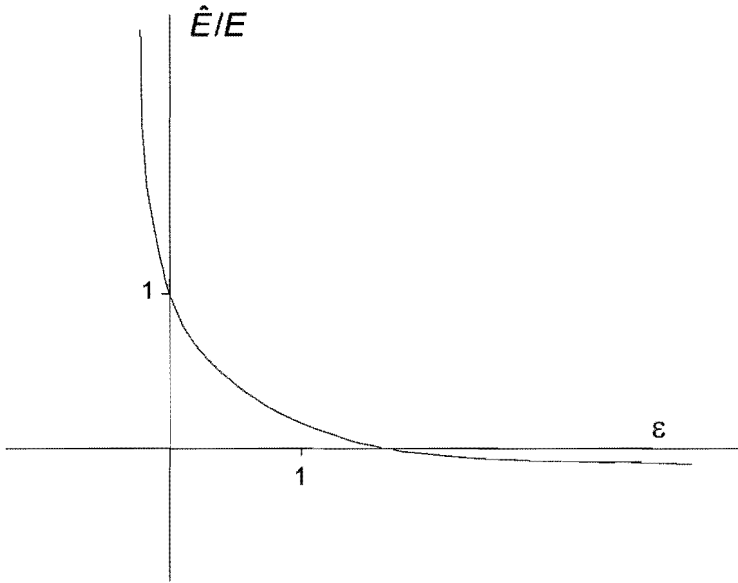
The maximum remains even when you plot σ versus ε_t . You will then get: $\frac{\sigma}{E} = \varepsilon_t e^{-\varepsilon_t}$



The modulus is defined as: $E = \frac{\sigma_t}{\varepsilon_t}$, but in terms of σ and ε this becomes:

$$\hat{E} = \frac{d\sigma}{d\varepsilon} = E \frac{1 - \ln(1 + \varepsilon)}{(1 + \varepsilon)^2}$$

Plotting $\frac{\hat{E}}{E}$ vs. ε then gives:



The modulus seems to increase during compression, and seems to decrease (and even become negative) during tension. These are all artefacts from the definitions of σ and ε .

Appendix C

Examples of towers

In order to show some practical applications of material properties, we will look at two constructions that go to the limit.

Example 1: Brick tower

Brick has a density of 2000 kg/m^3 , and therefore applies a pressure downwards per meter of height of 19600 Pa ($= \rho g$) on the underlying brick. The compression strength (σ_c) of brick is 40 MPa , so the maximum height of a brick tower with constant cross-sectional area is:

$$h_{\max} = \frac{\sigma_c}{\rho g} = 40 \times 10^6 / 19600 = 2 \text{ km}$$

When the tower is higher, the pressure on the lowest layer of bricks (which carries the rest) is higher than the strength of the material, so the bottom layer will crumble. This is already a quite nice Tower of Babel.

The calculation becomes more complex when we want to build a pyramid instead of a straight tower: the lowest layer of bricks then carries a much lower weight. The maximum allowed pressure on the lowest layer is then:

$$\sigma_c = \frac{\rho g V}{A_g}$$

Here, V is the volume of the tower, and A_g is the ground surface area. We can then write:

$$\frac{V}{A_g} = \frac{\sigma_c}{\rho g} = 2 \text{ km}$$

When we build a pyramid of height h , we get: $V = A_g h / 3$, so:

$$h_{\max} = 6 \text{ km}$$

This is quite close to the actual height of Mount Everest (rock instead of brick), and also explains why it is no surprise that the pyramid has been invented a number of times in different places and times.

Example 2: Space elevator

For a satellite of mass m moving in a stable orbit of radius r with an angular speed ω around the Earth, there must be a centripetal force ($F_c = m\omega^2 r$) which is due to the gravitational force between the satellite and the Earth ($F_g = GM_\oplus m/r^2$).

A geostationary satellite always hangs over the same point of the equator, so it must have a revolution time of 24 hours. With $G = 6.67 \cdot 10^{-11} \text{ Nm}^2\text{kg}^{-2}$, mass of the Earth $M_\oplus = 6 \cdot 10^{24} \text{ kg}$ and $\omega = 2\pi/(24 \times 3600) = 7.3 \cdot 10^{-5} \text{ rad/s}$, the geostationary orbit has a radius:

$$r_s = \left(\frac{GM_\oplus}{\omega^2} \right)^{1/3} = 4.23 \cdot 10^7 \text{ m} = 42300 \text{ km}$$

Since the Earth itself has a radius $r_\oplus = 6.4 \cdot 10^6 \text{ m}$, the height above the Earth's surface then is:

$$h_s = r_s - r_\oplus = 36000 \text{ km}$$

From such a satellite, one can lower a cable to the Earth's surface, as long as a cable is also deployed on the other side of the satellite (away from the Earth), in order to keep the centre of mass in the geostationary orbit. Then, one can use a simple elevator system along the cable to go to space: the space elevator. Rockets will no longer be necessary.

The only problem is: can a cable that is 36000 km long or more carry its own weight? This problem is more complex than the tower in the previous case, since the value of the acceleration g is not constant anymore.

Let's assume that we use a cable with constant cross-sectional area A . On each small piece of the cable with length dr , at a radius r from the centre of the Earth, there are stresses in the cable towards the Earth, $\sigma(r)$, and away from the Earth, $\sigma(r + dr)$. Now, the centripetal force must be generated by the gravitational force and these stresses:

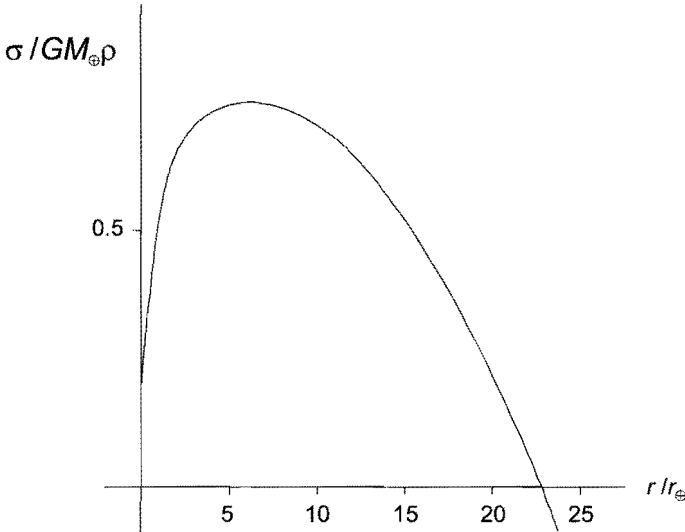
$$F_c = \omega^2 r A \rho dr = F_g + \sigma(r)A - \sigma(r + dr)A$$

$$\text{This gives: } \frac{\sigma(r + dr) - \sigma(r)}{dr} = \frac{d\sigma}{dr} = \frac{GM_\oplus \rho}{r^2} - \omega^2 \rho r$$

The maximum stress in the cable is reached when $\frac{d\sigma}{dr} = 0$, so at $r = r_s$. This means that the entire weight of the cable hangs from its point in the geostationary orbit. When we use the boundary condition that the cable end at the Earth's surface must hang free without stress ($\sigma(r_\oplus) = 0$), we get:

$$\sigma(r) = GM_\oplus \rho \left(\frac{1}{r_0} - \frac{1}{r} + \frac{r_\oplus^2 - r^2}{2r_s^3} \right)$$

When we now plot $\frac{\sigma}{GM_{\oplus}\rho}$ vs. $\frac{r}{r_{\oplus}}$, we get the following curve:



The total length of the cable (L) now follows from the boundary condition that the other end of the cable must also hang free in space without stress:

$$\sigma(r_{\oplus} + L) = 0$$

After some number crunching, this gives: $L = 144000$ km, or 101700 km outside of the geostationary orbit and 42300 km within the orbit down to the surface. The total mass required for this cable is $AL\rho$.

If we go back to the maximum stress that the material has to carry, we see that:

$$\sigma_{\max} = \sigma(r_s) = 48.4\rho \text{ MPa}$$

For realistic materials, the value of $\frac{\sigma_{\max}}{\rho}$ is on the order of 1–2 MPa/kg·m⁻³, so we can not directly start to build the space elevator.

An obvious solution is of course to make the cross-sectional area of the cable large in the geostationary orbit (where the highest load is carried), and smaller elsewhere in order to decrease the mass to carry. We can e.g. choose to keep the stress constant everywhere in the cable. Then it turns out that we have to use a cross-sectional area with an exponential decrease when we move away from the geostationary orbit. When we use carbon fibres as material (very high $\frac{\sigma_{\max}}{\rho}$), we can

build a realistic space elevator with a cross-sectional area that is 10 times smaller on the Earth's surface than in geostationary orbit.

Appendix D Literature

- J.E. Gordon, *The new science of strong materials* (HAB76GOR): Very good explanation of the principles of materials science.
- J.E. Gordon, *Structures* (FEB91GOR): Application of materials science in constructions; does not really belong to the topics in this book, but is very readable.
- J. Vincent, *Structural biomaterials* (PCW90VIN): Biological materials seen in a mechanical way; very good overview.
- S.A. Wainwright *et al.*, *Mechanical design in organisms* (PCW76MEC): Good overview of the mechanical properties of various biological materials; goes on with structures in organisms.
- J.B. Park & R.S. Lakes, *Biomaterials* (PCW92PAR): Properties of various biomaterials.
- L.V. Interrante & M.J. Hampden-Smith, *Chemistry of advanced materials*, Ch. 11: C.C. Perry, *Biomaterials* (HDS98CHE): Recent developments concerning biomaterials.
- Van der Vegt, *Polymeren: van keten tot kunststof* (HSB96VEG); in Dutch, good overview of polymers.
- R. Young, *Introduction to Polymers* (HSB91YOU): More thorough than van der Vegt on polymers.
- P. Ball, *Made to measure* (HAB97BAL): Readable account of recent developments in materials science.
- D. Bloor *et al.*, *Encyclopedia of advanced materials* (4 parts, HAA94ENC): An encyclopaedia, need I say more?
- Y. Fung, *Biomechanics—Mechanical properties of living tissues* (PFE93FUN): Contains a more elaborate section on visco-elasticity, bone and muscle.

Appendix E

Selected material properties

Table 1. Modulus of elasticity (E), shear modulus (G), Poisson ratio (ν), density (ρ), and reduced modulus (E/ρ) of various materials at room temperature

	E [GPa]	G [GPa]	ν [-]	ρ [Mg/m ³]	E/ρ [MNm/kg]
<i>Ceramics</i>					
NaCl	49			2.17	22.6
LiF	112				
MgO	293				
SiO ₂	94	37.6	0.25	2.6	36.2
Pyrex glass	69	28.8	0.20	2.23	30.9
Al ₂ O ₃	390	154.8	0.26	3.9	100
ZrO ₂	200			5.8	34.5
Fireclay brick	97			1.5–1.8	
<i>Covalently bound ceramics</i>					
Si ₃ N ₄	310			3.2	
SiC	450			2.9	155
TiC	379			7.2	52.6
WC	550	225.4	0.22	15.5	35.5
Diamond	1050		0.20	3.51	285
Si	166				
Ge	129				
<i>Metals</i>					
Al	70	26.3	0.33	2.7	25.9
Al-alloys	72.4	27.6	0.31	2.7	26.8
Cu	115			8.94	12.9
Cu-alloys	117	44	0.33	8.9	13.1
Ni	207	77.7	0.30	8.9	23.2
Fe	205			7.87	26.0
Steels	207	77.7	0.33	7.8	26.5
Stainless steel	193	65.6	0.28	7.9	24.4
Ti	110	44.8	0.31	4.5	24.4
W	384	157	0.27	19.3	20
<i>Polymers</i>					
PE	0.4–1.3		0.4	0.91–0.97	ca. 0.96
PMMA	2.4–3.4			1.2	ca. 2.4
PS	2.7–4.2		0.4	1.1	ca. 3.2
Nylon	1.2		0.4	1.2	ca. 1
Rubbers	0.01–0.1		0.49	1.2–1.6	
<i>Various</i>					
Concrete–cement	45–50		0.20	2.5	ca. 19
Common bricks	10–17				
Common wood					
(grain)	9–16			0.4–0.8	ca. 20
(⊥ grain)	0.6–1.0			0.4–0.8	ca. 1.3
Granite	40			2.4	

Table 2. Typical values for plastic deformation ($\sigma_T = K_{pl}\epsilon_T^N$) of metals at room temperature

	K_{pl} [MPa]	N [-]
Al Alloys		
1100, annealed	180	0.20
2024, hardened	690	0.16
6061, annealed	205	0.20
6061, hardened	410	0.05
7075, annealed	400	0.17
Brass (Cu–Zn)		
70–30, annealed	895	0.49
85–15, cold-rolled	580	0.34
Bronze (Cu–Sn), annealed	720	0.46
Co-alloy	2070	0.50
Cu, annealed	315	0.54
Mo, annealed	725	0.13
Steel		
low-carbon, annealed	530	0.26
1045, hot-rolled	965	0.14
4135, annealed	1015	0.17
4135, cold-rolled	1100	0.14
4340, annealed	640	0.15
52100, annealed	1450	0.07
302, stainless, annealed	1300	0.30
304 stainless, annealed	1275	0.45
410 stainless, annealed	960	0.10

Table 3. Slip systems and critical shearing stress (τ_C) in crystals

	τ_C [MPa]	Slip plane	Slip direction
FCC (12 slip systems)		{111}	$\langle 1\bar{1}0 \rangle$
Ag (99.99%)	0.58		
Cu (99.999%)	0.65		
Ni (99.8%)	5.7		
Diamond cubic (12 slip systems)		{111}	$\langle 1\bar{1}0 \rangle$
Si, Ge			
BCC (12 slip systems)		{110}	$\langle 1\bar{1}1 \rangle$
Fe (99.96%)	27.5		
Mo	49.0		
HCP (3 slip systems)		{0001}	$\langle 11\bar{2}0 \rangle$
Zn (99.999%)	0.18		
Cd (99.996%)	0.58		
Mg (99.996%)	0.77		
Al ₂ O ₃ , BeO			
Rock salt (6 slip systems)		(110)	$[1\bar{1}0]$
LiF, MgO			

Table 4. Mechanical properties of polymers

	E [GPa]	ρ [Mg/m ³]	σ_Y [MPa]	T_g [°C]
<i>Thermoplastics</i>				
High-density PE	0.56	0.96	30	
Low-density PE	0.18	0.91	11	-20
PVC	2.0	1.2	25	80
PP	1.3	0.9	35	0
PS	2.7	1.1	50	100
Polycarbonate (PC)	2.5	1.2-1.3	68	150
PET	8	0.94	135	67
PMMA	2.8	1.2	70	100
Polyesters	1.3-4.5	1.1-1.4	65	67
Polyamide	2.8	1.1-1.2	70	60
Teflon	0.4	2.3	25	120
<i>Thermosets</i>				
Epoxies	2.1-5.5	1.2-1.4	60	107-200
Phenolics	18	1.5	80	200-300
Polyesters	14	1.1-1.5	70	200
Polyimides	21	1.3	190	350
Silicones	8	1.25	40	300
Ureas	7	1.3	60	80
Urethanes	7	1.2-1.4	70	100

Table 5. Toughness of some materials

	K_{1C} [MPa·m ^{1/2}]
<i>Metals</i>	
Al	45
Al 2024, hardened	26
Al 2024, annealed	44
Al 7075, hardened	26
Ti-6Al-4V	55
Mild steel	140
Steel 4340, hardened	60.4
Steel 4340, annealed	99
Maraging steel	ca. 133
Pressure vessel steel	200
<i>Ceramics</i>	
Soda glass	0.7
Al ₂ O ₃	3.7
SiO ₂	1
SiC	3.1
Si ₃ N ₄	4
WC	80
TiC	0.5
ZrO ₂ , stabilized	12
Concrete	0.2
<i>Polymers</i>	
High density PE	ca. 2
PMMA	ca. 1.3
PS	ca. 1
Polycarbonate (PC)	2
Epoxy	ca. 0.5
Fibreglass reinforced epoxy	ca. 40

Table 6. Mechanical properties of metals

		σ_T [MPa]	σ_Y [MPa]	Ductility (%elong.)
<i>Plain carbon steel</i>				
1020 (0.20C, 0.45Mn)	as rolled	448	331	36
	annealed	393	297	36
1040 (0.40C, 0.75Mn)	as rolled	621	414	25
	annealed	517	352	30
	hardened	800	593	20
1080 (0.80C, 0.75Mn)	as rolled	967	586	12
	annealed	614	373	25
	hardened	1304	980	1
<i>Low alloy steel</i>				
4340 (0.40C, 0.90Mn, 0.80Cr, 1.83Ni)	annealed	745	469	22
	hardened	1725	1587	10
5160 (0.60C, 0.80Cr, 0.90Mn)	annealed	725	276	17
	hardened	2000	1773	9
8650 (0.50C, 0.55Ni, 0.50Cr)	annealed	710	386	22
	hardened	1725	1552	10
<i>Stainless steel</i>				
430 (17Cr, 0.12C max, ferritic)		550	375	25
304 (19Cr, 9Ni, austenitic)		579	290	55
<i>Wrought aluminium alloys</i>				
1100 (99.0 min Al, 0.12Cu)	annealed	89	24	25
	half-hard	124	97	4
2024 (4.4Cu, 1.5Mg, 0.6Mn)	annealed	220 (max)	97 (max)	12
	heat-treated	500	390	5
6061 (1.0Mg, 0.6Si, 0.27Cu, 0.2Cr)	annealed	152 (max)	82 (max)	16
	heat-treated	315	280	12
7075 (5.6Zn, 2.5Mg, 1.6Cr, 0.23Cr)	annealed	276 (max)	145 (max)	10
	heat-treated	570	500	8
<i>Cast aluminium alloys</i>				
356 (7Si, 0.3Mg)	sand-cast	207 (min)	138 (min)	3
	heat-treated	229 (min)	152 (min)	3
413 (12Si, 2Fe)	die cast	297	145	2.5
<i>Wrought copper alloys</i>				
OFHC (99.99Cu)	annealed	220	69	45
	cold worked	345	310	6
Electrolytic tough pitch (0.04O)	annealed	220	69	45
	cold worked	345	310	6
Brass (70Cu, 30Zn)	annealed	325	105	62
	cold worked	525	435	8
Beryllium copper (1.7Be, 0.20Co)	solution treated	410	190	60
	hardened	1240	1070	4
<i>Casting copper alloys</i>				
Leaded bronze (5Sn, 5Pb, 5Zn)	as cast	255	117	30
Aluminium bronze (4Fe, 11Al)	as cast	586	242	18

Table 7. Properties of reinforcing fibres, matrices, and composites

	ρ [Mg/m ³]	E [GPa]	σ_T [GPa]	K_{1C} [MPa·m ^{1/2}]
<i>Fibre</i>				
E-glass (10 μ m)	2.56	76	1.4–2.5	
High-modulus carbon (8 μ m)	1.75	390	2.2	
High strength carbon (8 μ m)	1.95	250	2.7	
Kevlar (12 μ m)	1.45	125	3.2	
SiC whisker	3.2	480	3	
SiC fibre (140 μ m)	3.0	420	3.9	
Al ₂ O ₃ (3 μ m)	3.2	100	1.0	
Si ₃ N ₄	3.2	380	2	
Boron (100–200 μ m)	2.6	380	3.8	
<i>Matrix</i>				
Epoxy	1.2–1.4	2.1–5.5	0.063	
Polyester	1.1–1.4	1.3–4.5	0.060	
<i>Composites</i>				
CFRP (85% C-fibre in epoxy)	1.5	189	1.05	32–45
GFRP (50% glass in polyester)	2	48	1.24	42–60
KFRP (60% Kevlar fibre in epoxy)	1.4	76	1.24	
2014–Al (20% Al ₂ O ₃ , particulate)		103	0.48	
2124–Al (30% SiC, particulate)		130	0.69	
6061–Al		69	0.31	
6061–Al (51% B, continuous fibre)		231	1.42	
6061–Al (20% SiC, discontinuous fibre)		115	0.48	
Si ₃ N ₄ (10% SiC whisker)			0.45	
Al ₂ O ₃ (10% SiC whisker)			0.45	

Appendix F
Non-SI units*Length:*

1 inch (1 in. or 1") = 2.54 cm

1 foot (1 ft or 1') = 0.305 m

1 Ångström (1 Å) = 0.1 nm

Force:

1 pound-force (1 lbf) = 4.448 N

1 kilogram-force (1 kgf) = 9.808 N

1 dyne = 10 μ N*Mass:*

1 pound-mass (1 lbm) = 0.454 kg

Pressure/stress:

1 psi (pound-force per square inch) = 6.90 kPa

1 ksi = 1000 psi

Energy:

1 cal (calorie) = 4.184 J

1 erg = 0.1 μ J

1 Btu (British thermal unit) = 1054 J

Power:

1 hp (horse power) = 746 W

Temperature: $T/K = t/^{\circ}\text{C} + 273.15$ $t/^{\circ}\text{F} = (9/5) \times (t/^{\circ}\text{C}) + 32$ *Molar mass:*1 Da (dalton) = 1 g/mol = 10^{-3} kg/mol

Appendix G
Periodic table; Physical constants; Properties of elements

H 1																		He 2
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10	
Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18	
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36	
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54	
Cs 55	Ba 56	Lu 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86	
Fr 87	Ra 88	Lr 103	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111								
		La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70			
		Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102			

Physical constants

(\$ = Only in Appendices)

$$\epsilon_0 = 8.85419 \times 10^{-12} \text{ F/m}$$

$$e = 1.6021765 \times 10^{-19} \text{ C}$$

$$N_A = 6.02214 \times 10^{23} \text{ mol}^{-1}$$

$$G = 6.67 \times 10^{-11} \text{ Nm}^2\text{kg}^{-2} \text{ ($)}$$

$$g = 9.81 \text{ m/s}^2 \text{ ($)}$$

$$k_B = 1.38066 \times 10^{-23} \text{ J/K ($)}$$

$$M_{\oplus} = 6 \times 10^{24} \text{ kg ($)}$$

Properties of elements at 25 °C and 1 bar (unless stated otherwise)

Ionic radius can be dependent on coordination number:

→ zinc blende = 4, rock salt = 6, CsCl = 8. (See Appendix L for more information.)

Atomic radius: half the bond between an element and itself.

a/p = atoms per point for cubic or hexagonal structures.

Element	Molar mass /g·mol ⁻¹	Ionic radius/nm (charge, coordination)	Atomic radius /nm	Crystal Structure	Lattice parameter cubic-hex a, c/nm	Solid or liquid density /Mg·m ⁻³	a/p
Actinium (₈₉ Ac)	227.07	0.112 (3+,6)	0.188	FCC	0.5311	10.06	1
Aluminium (₁₃ Al)	26.98	0.039 (3+,4) 0.054 (3+,6)	0.143	FCC	0.4050	2.70	1
Americium (₉₅ Am)	243.06	0.098 (3+,4) 0.109 (3+,6)	0.173	HCP	0.347, 1.124	13.67	4
Antimony (₅₁ Sb)	112.76	0.076 (3+,6) 0.060 (5+,6)	0.141	rhomb	–	6.69	–
Argon (₁₈ Ar)	39.95	–	–	gas	–	–	–
Arsenic (₃₃ As)	74.92	0.058 (3+,6) 0.034 (5+,4) 0.046 (5+,6)	0.125	rhomb	–	5.72	–
Astatine (₈₅ At)	209.99	?	0.140	?	?	?	?
Barium (₅₆ Ba)	137.33	0.135 (2+,6) 0.142 (2+,8)	0.217	BCC	0.5019	3.5	1
Berkelium (₉₇ Bk)	247.07	0.096 (3+,6)	0.172	HCP	0.342, 1.107	14.79	4
Beryllium (₄ Be)	9.012	0.027 (2+,4) 0.045 (2+,6)	0.114	HCP	0.229, 0.358	1.85	2
Bismuth (₈₃ Bi)	208.98	0.103 (3+,6) 0.117 (3+,8) 0.076 (5+,6)	0.170	rhomb	–	9.75	–
Bohrium (₁₀₇ Bh)	262.12	?	?	?	?	≈ 37	?
Boron (₃ B)	10.81	0.023 (3+)	0.097	rhomb	–	2.34	–
Bromine (₃₅ Br)	79.90	0.196 (1–,6) 0.025 (7+,4) 0.039 (7+,6)	0.119	liquid	–	3.14	–
Cadmium (₄₈ Cd)	112.41	0.078 (2+,4) 0.095 (2+,6) 0.110 (2+,8)	0.148	HCP	0.298, 0.562	8.65	2
Calcium (₂₀ Ca)	40.08	0.100 (2+,6) 0.112 (2+,8)	0.197	FCC	0.5582	1.55	1
Californium (₉₈ Cf)	251.08	0.095 (3+,6)	0.199	HCP	0.339, 1.102	?	4
Carbon (₆ C)	12.011	0.015 (4+,4) 0.016 (4+,6)	0.077	HCP HAX	0.246, 0.671	2.25	4
Carbon (> 60 GPa)	idem	idem	idem	FCC	0.3567	3.51	2

Element	Molar mass /g·mol ⁻¹	Ionic radius/nm (charge, coordination)	Atomic radius /nm	Crystal Structure	Lattice parameter cubic-hex a, c/nm	Solid or liquid density /Mg·m ⁻³	a/p
Cerium (₅₈ Ce)	140.12	0.101 (3+,6) 0.114 (3+,8)	0.183	HCP	0.368, 1.186	6.75	4
Caesium (₅₅ Cs)	132.91	0.167 (1+,6) 0.174 (1+,8)	0.263	BCC	0.6080	1.87	1
Chlorine (₁₇ Cl)	35.45	0.181 (1-,6) 0.008 (7+,4)	0.107	gas	–	–	–
Chromium (₂₄ Cr)	52.00	0.062 (3+,6) 0.026 (6+,4) 0.044 (6+,6)	0.125	BCC	0.2885	7.19	1
Cobalt (₂₇ Co)	58.93	0.056 (2+,4) 0.065 (2+,6) 0.090 (2+,8) 0.055 (3+,6)	0.125	HCP	0.251, 0.407	8.85	2
Copper (₂₉ Cu)	63.55	0.060 (1+,4) 0.077 (1+,6) 0.073 (2+,6)	0.128	FCC	0.3615	8.94	1
Curium (₉₆ Cm)	247.07	0.097 (3+,6)	0.174	HCP	0.350, 1.133	13.30	4
Darmstadtium (₁₁₀ Ds)	ca. 281	?	?	?	?	?	?
Dubnium (₁₀₅ Db)	262.11	?	?	?	?	29.00	?
Dysprosium (₆₆ Dy)	162.50	0.091 (3+,6) 0.103 (3+,8)	0.175	HCP	0.359, 0.565	8.55	2
Erbium (₆₈ Er)	167.26	0.089 (3+,6) 0.100 (3+,8)	0.173	HCP	0.356, 0.559	9.07	2
Europium (₆₃ Eu)	151.97	0.095 (3+,6) 0.107 (3+,8)	0.204	BCC	0.4583	5.24	1
Fermium (₁₀₀ Fm)	257.10	?	?	?	?	?	?
Fluorine (₉ F)	19.00	0.133 (1-,6)	0.0709	gas	–	–	–
Francium (₈₇ Fr)	223.02	0.180 (1+,6)	0.270	?	?	?	?
Gadolinium (₆₄ Gd)	157.25	0.094 (3+,6) 0.105 (3+,8)	0.179	HCP	0.364, 0.578	7.90	2
Gallium (₃₁ Ga)	69.72	0.047 (3+,4) 0.062 (3+,6)	0.135	ortho	–	5.91	–
Germanium (₃₂ Ge)	72.59	0.073 (2+,6) 0.039 (4+,4) 0.053 (4+,6)	0.122	FCC	0.5658	5.32	2
Gold (₇₉ Au)	196.97	0.137 (1+,6) 0.085 (3+,6)	0.144	FCC	0.4079	19.3	1
Hafnium (₇₂ Hf)	178.49	0.058 (4+,4) 0.071 (4+,6) 0.083 (4+,8)	0.157	HCP	0.319, 0.505	13.31	2
Hassium (₁₀₈ Hs)	≈ 265	?	?	?	?	≈ 41	?
Helium (₂ He)	4.003	–	–	gas	–	–	–

Element	Molar mass /g·mol ⁻¹	Ionic radius/nm (charge, coordination)	Atomic radius /nm	Crystal Structure	Lattice parameter cubic-hex a, c/nm	Solid or liquid density /Mg·m ⁻³	a/p
Holmium (₆₇ Ho)	164.93	?	0.147	HCP	0.358, 0.562	8.80	2
Hydrogen (₁ H)	1.008	–	0.0373	gas	–	–	–
Indium (₄₉ In)	114.82	0.062 (3+,4) 0.080 (3+,6)	0.166	tetra	–	7.31	–
Iodine (₅₃ I)	126.91	0.220 (1–,6) 0.095 (5+,6) 0.042 (7+,4) 0.053 (7+,6)	0.136	ortho	–	4.94	–
Iridium (₇₇ Ir)	192.22	0.068 (3+,6)	0.135	FCC	0.3839	22.56	1
Iron (₂₆ Fe)	55.85	0.063 (2+,4) 0.061 (2+,6) 0.092 (2+,8) 0.049 (3+,4) 0.055 (3+,6) 0.078 (3+,8)	0.124	BCC	0.2866	7.87	1
Iron (> 912 °C)	idem	idem	idem	FCC	0.3647	?	1
Krypton (₃₆ Kr)	83.80	–	–	gas	–	–	–
Lanthanum (₅₇ La)	138.91	0.103 (3+,6) 0.116 (3+,8)	0.188	HCP	0.377, 1.217	6.15	4
Lawrencium (₁₀₃ Lr)	262.11	?	?	?	?	?	?
Lead (₈₂ Pb)	207.2	0.119 (2+,6) 0.129 (2+,8) 0.065 (4+,4) 0.078 (4+,6) 0.094 (4+,8)	0.175	FCC	0.4950	11.3	1
Lithium (₃ Li)	6.94	0.059 (1+,4) 0.076 (1+,6) 0.092 (1+,8)	0.152	BCC	0.3509	0.53	1
Lutetium (₇₁ Lu)	174.97	0.086 (3+,6) 0.097 (3+,8)	0.172	HCP	0.351, 0.555	9.84	2
Magnesium (₁₂ Mg)	24.31	0.057 (2+,4) 0.072 (2+,6) 0.089 (2+,8)	0.160	HCP	0.321, 0.521	1.74	2
Manganese (₂₅ Mn)	54.94	0.066 (2+,4) 0.083 (2+,6) 0.096 (2+,8) 0.058 (3+,6) 0.039 (4+,4) 0.053 (4+,6) 0.033 (5+,4) 0.026 (6+,4) 0.025 (7+,4)	0.112	BCC	0.8914	7.43	29

Element	Molar mass /g·mol ⁻¹	Ionic radius/nm (charge, coordination)	Atomic radius /nm	Crystal Structure	Lattice parameter cubic-hex a, c/nm	Solid or liquid density /Mg·m ⁻³	a/p
Meitnerium (109Mt)	276.15	?	?	?	?	?	?
Mercury (80Hg)	200.59	0.119 (1+,6) 0.096 (2+,4) 0.102 (2+,6) 0.114 (2+,8)	0.150	liquid	–	14.2	–
Molybdenum (42Mo)	95.94	0.069 (3+,6) 0.065 (4+,6) 0.046 (5+,4) 0.061 (5+,6) 0.041 (6+,4) 0.059 (6+,6)	0.136	BCC	0.3147	10.2	1
Neodymium (60Nd)	144.24	0.098 (3+,6) 0.112 (3+,8)	0.181	HCP	0.366, 1.180	7.01	4
Neon (10Ne)	20.18	–	–	gas	–	–	–
Neptunium (93Np)	237.05	0.101 (3+,6)	0.155	ortho	–	20.25	–
Nickel (28Ni)	58.69	0.069 (2+,6) 0.056 (3+,6)	0.125	FCC	0.3524	8.9	1
Niobium (41Nb)	92.91	0.072 (3+,6) 0.079 (3+,8) 0.068 (4+,6) 0.048 (5+,4) 0.064 (5+,6) 0.074 (5+,8)	0.143	BCC	0.3307	8.6	1
Nitrogen (7N)	14.007	0.016 (3+,6) 0.013 (5+,6)	0.071	gas	–	–	–
Nobelium (102No)	259.10	?	?	?	?	?	?
Osmium (76Os)	190.23	0.063 (4+,6) 0.058 (5+,6) 0.055 (6+,6) 0.039 (8+,4)	0.134	HCP	0.273, 0.439	22.59	2
Oxygen (8O)	16.00	0.140 (2–,6) 0.142 (2–,8)	0.060	gas	–	–	–
Palladium (46Pd)	106.42	0.086 (2+,6) 0.076 (3+,6) 0.062 (4+,6)	0.138	FCC	0.3890	12.02	1
Phosphorus (15P)	30.97	0.017 (5+,4) 0.038 (5+,6)	0.109	ortho	–	1.83	–
Platinum (78Pt)	195.08	0.080 (2+,6) 0.063 (4+,6)	0.139	FCC	0.3924	21.4	1
Plutonium (94Pu)	244.06	0.100 (3+,6)	0.159	monocl	–	19.84	–
Polonium (84Po)	208.98	0.097 (4+,6)	0.140	SC	0.3366	9.32	1
Potassium (19K)	39.10	0.137 (1+,4) 0.138 (1+,6) 0.151 (1+,8)	0.231	BCC	0.5344	0.86	1

Element	Molar mass /g·mol ⁻¹	Ionic radius/nm (charge, coordination)	Atomic radius /nm	Crystal Structure	Lattice parameter cubic-hex a, c/nm	Solid or liquid density /Mg·m ⁻³	a/p
Praseodymium (59Pr)	140.91	0.099 (3+,6) 0.113 (3+,8)	0.182	HCP	0.367, 1.183	6.77	4
Promethium (61Pm)	144.91	0.097 (3+,6) 0.109 (3+,8)	0.183	HCP	0.365, 1.165	7.22	4
Protactinium (91Pa)	231.04	0.104 (3+,6)	0.156	tetra	–	15.37	–
Radium (88Ra)	226.03	0.148 (2+,8)	0.220	BCC	0.5148	≈ 5.0	1
Radon (86Rn)	222.02	–	–	gas	–	–	–
Rhenium (75Re)	186.21	0.063 (4+,6) 0.058 (5+,6) 0.055 (6+,6) 0.038 (7+,4) 0.053 (7+,6)	0.137	HCP	0.276, 0.446	21.02	2
Rhodium (45Rh)	102.91	0.067 (3+,6) 0.060 (4+,6) 0.055 (5+,6)	0.134	FCC	0.3803	12.41	1
Roentgenium (111Rg)	ca. 280	?	?	?	?	?	?
Rubidium (37Rb)	85.47	0.152 (1+,6) 0.161 (1+,8)	0.244	BCC	0.5705	1.53	1
Rutherfordium (104Rf)	261.11	?	?	?	?	≈ 23	?
Samarium (62Sm)	150.36	0.119 (2+,6) 0.127 (2+,8) 0.096 (3+,6) 0.108 (3+,8)	0.180	rhomb	–	7.52	–
Scandium (21Sc)	44.96	0.075 (3+,6) 0.087 (3+,8)	0.160	HCP	0.331, 0.527	2.99	2
Seaborgium (106Sg)	263.12	?	?	?	?	≈ 35	?
Selenium (34Se)	78.96	0.198 (2-,6) 0.050 (4+,6) 0.028 (6+,4) 0.042 (6+,6)	0.117	HCP hex	0.437, 0.495	4.79	3
Silicon (14Si)	28.09	0.026 (4+,4) 0.040 (4+,6)	0.117	FCC	0.5431	2.33	2
Silver (47Ag)	107.87	0.100 (1+,4) 0.115 (1+,6) 0.128 (1+,8)	0.144	FCC	0.4086	10.5	1
Sodium (11Na)	22.99	0.098 (1+,4) 0.102 (1+,6) 0.118 (1+,8)	0.186	BCC	0.4291	0.97	1
Strontium (38Sr)	87.62	0.118 (2+,6) 0.126 (2+,8)	0.215	FCC	0.6084	2.54	1
Sulphur (16S)	32.06	0.184 (2-,6) 0.037 (4+,6) 0.012 (6+,4) 0.029 (6+,6)	0.104	ortho	–	2.07	–

Element	Molar mass /g·mol ⁻¹	Ionic radius/nm (charge, coordination)	Atomic radius /nm	Crystal Structure	Lattice parameter cubic-hex a, c/nm	Solid or liquid density /Mg·m ⁻³	a/p
Tantalum (₇₃ Ta)	180.95	0.072 (3+,6) 0.068 (4+,6) 0.064 (5+,6)	0.143	BCC	0.3303	16.65	1
Technetium (₄₃ Tc)	98.91	0.065 (4+,6)	0.135	HCP	0.274, 0.439	≈ 11.5	2
Tellurium (₅₂ Te)	127.60	0.221 (2-,6) 0.066 (4+,4) 0.097 (4+,6) 0.043 (6+,4) 0.056 (6+,6)	0.137	HCP HEX	0.446, 0.593	6.24	3
Terbium (₆₅ Tb)	158.93	0.092 (3+,6) 0.104 (3+,8)	0.176	HCP	0.361, 0.570	8.23	2
Thallium (₈₁ Tl)	204.38	0.150 (1+,6) 0.159 (1+,8) 0.075 (3+,4) 0.089 (3+,6) 0.098 (3+,8)	0.171	HCP	0.346, 0.552	11.85	2
Thorium (₉₀ Th)	232.04	0.094 (4+,6) 0.105 (4+,8)	0.180	FCC	0.5084	11.72	1
Thulium (₈₉ Tm)	168.93	0.088 (3+,6) 0.099 (3+,8)	0.172	HCP	0.354, 0.555	9.32	2
Tin (₅₀ Sn)	118.69	0.055 (4+,4) 0.069 (4+,6) 0.081 (4+,8)	0.158	tetra	–	7.30	–
Tin (< 13 °C)	idem	idem	idem	FCC	0.6489	5.75	2
Titanium (₂₂ Ti)	47.88	0.086 (2+,6) 0.067 (3+,6) 0.042 (4+,4) 0.061 (4+,6) 0.074 (4+,8)	0.147	HCP	0.295, 0.468	4.51	2
Tungsten (₇₄ W)	183.85	0.066 (4+,6) 0.062 (5+,6) 0.042 (6+,4) 0.060 (6+,6)	0.137	BCC	0.3165	19.3	1
Uranium (₉₂ U)	238.03	0.089 (4+,6) 0.100 (4+,8)	0.138	ortho	–	19.0	–
Vanadium (₂₃ V)	50.94	0.079 (2+,6) 0.064 (3+,6) 0.058 (4+,6) 0.072 (4+,8) 0.036 (5+,4) 0.054 (5+,6)	0.132	BCC	0.3028	6.1	1
Xenon (₅₄ Xe)	131.29	–	–	gas	–	–	–
Ytterbium (₇₀ Yb)	173.04	0.102 (2+,6) 0.114 (2+,8) 0.099 (3+,8)	0.194	FCC	0.5485	6.97	1
Yttrium (₃₉ Y)	88.91	0.090 (3+,6) 0.102 (3+,8)	0.180	HCP	0.365, 0.573	4.47	2

Element	Molar mass /g·mol ⁻¹	Ionic radius/nm (charge, coordination)	Atomic radius /nm	Crystal Structure	Lattice parameter cubic-hex a, c/nm	Solid or liquid density /Mg·m ⁻³	a/p
Zinc (₃₀ Zn)	65.39	0.060 (2+,4) 0.074 (2+,6) 0.090 (2+,8)	0.133	HCP	0.266, 0.495	7.13	2
Zirconium (₄₀ Zr)	91.22	0.059 (4+,4) 0.072 (4+,6) 0.084 (4+,8)	0.158	HCP	0.323, 0.515	6.49	2

Appendix H Rubber elasticity

For a material that is being deformed (L increases due to force F) we can write for the change in internal energy: $dU = \delta Q - \delta W = TdS - FdL$.

This can also be written as: $F = \left(\frac{\partial U}{\partial L}\right) - T\left(\frac{\partial S}{\partial L}\right)$

The first term is familiar: it is the change in internal energy due to stretching of bonds between atoms. This leads to the Hookean behaviour we saw in Chapter 3.

The second term is a different form of elasticity, which is usually called rubber elasticity. In order to explain this we must first look at the entropy of a rubber.

For a polymer chain that is folded randomly, we can use the random-coil model to determine the entropy: there is a distribution function $W(x,y,z)$ (see Appendix N), and entropy is nothing more than this distribution written in different form:

$$S = k_B \ln W = C_S - k_B b_s^2 r_c^2 = C_S - k_B b_s^2 (x^2 + y^2 + z^2) \text{ [J/K]}$$

When we now deform the material in e.g. the z direction, we get a new dimension $z' = \lambda z$. With the usual assumption that the volume is constant (not always true!), we use: $V = xyz = x'y'z'$.

Then, there is equal contraction along the x and y directions: $x' = \frac{x}{\sqrt{\lambda}}$ and $y' = \frac{y}{\sqrt{\lambda}}$.

Then we can write for the change of entropy of a single polymer chain during this deformation:

$$\Delta S_{sc} = -k_B b_s^2 \left\{ x^2 \left(\frac{1}{\lambda} - 1 \right) + y^2 \left(\frac{1}{\lambda} - 1 \right) + z^2 (\lambda^2 - 1) \right\} \text{ [J/K]}$$

The material of course contains more polymer chains: N_c per m^3 . The density of the chains (dN_c) in a certain volume ($dx dy dz$) is the same as finding one chain end in a certain volume, so we can use the familiar distribution function again:

$$dN_c = N_c W(x,y,z) dx dy dz = N_c \left(\frac{b_s^2}{\pi^{3/2}} \right) e^{-b_s^2 r_c^2} dx dy dz$$

The total change of the entropy for all chains in $1 m^3$ is now the integral of $\Delta S_{sc} dN_c$. Fortunately this is a standard integral that can be calculated quite easily:

$$\Delta S_{ac} = -N_c k_B \left[\frac{\lambda^2 + \frac{2}{\lambda} - 3}{2} \right] \text{ [J/(K}\cdot\text{m}^3\text{)]}$$

This formula behaves as expected: for $\lambda > 1$ and $\lambda < 1$ we find $\Delta S < 0$, so stretching and compressing of the rubber network is less favourable as far as entropy is concerned.

When we have a piece of material with an initial length L_0 and initial cross section A_0 , we get as total entropy change for the whole chunk of polymer:

$$\Delta S_{\text{tot}} = -N_c k_B A_0 L_0 \left(\frac{\lambda^2 + \frac{2}{\lambda} - 3}{2} \right) \text{ [J/K]}$$

How do we translate this entropy change in the familiar terms of stress and strain?

For the stress we can write $\sigma = \frac{F}{A_0}$, and in a rubber (with very weak forces between

the chains) we can write as shown above: $F \approx -T \left(\frac{\partial S}{\partial L} \right)$

Since $\lambda = \frac{L}{L_0}$ this gives for the stress:

$$\sigma = - \left(\frac{T}{A_0} \right) \left(\frac{\partial S}{\partial \lambda} \right) \left(\frac{d\lambda}{dL} \right) = N_c k_B T \left(\lambda - \frac{1}{\lambda^2} \right)$$

Often it is written that $N_c k_B T = G$, the shear modulus of the rubber. Why this is done can be seen by the following arguments: first, there is a connection between the elongation factor λ and the strain ε :

$$\lambda = \frac{L}{L_0} = 1 + \varepsilon$$

For small values of ε ($\varepsilon \ll 1$) we can then approximately write:

$$\frac{1}{\lambda^2} = 1 - 2\varepsilon$$

Then the relation between σ and ε becomes:

$$\sigma = G(1 + \varepsilon - 1 + 2\varepsilon) = 3G\varepsilon$$

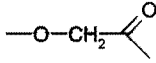
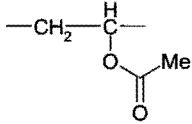
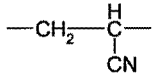
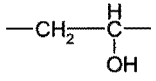
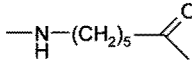
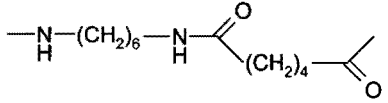
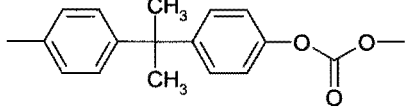
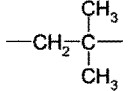
So: $G = \frac{E}{3}$. This is exactly what is expected for a rubber with a Poisson ratio (ν) of 0.5 (remember: constant volume was assumed).

For rubber elasticity we can then write:

$$\sigma = G \left(\lambda - \frac{1}{\lambda^2} \right)$$

Appendix I Polymer structures

Name	Abbreviation	Repeating unit
Poly(ethene)/poly(ethylene)	PE	$-\text{CH}_2\text{CH}_2-$
Poly(propene)/poly(propylene)	PP	$-\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{H}}{\text{C}}}-$
Poly(styrene)	PS	$-\text{CH}_2-\underset{\text{C}_6\text{H}_5}{\overset{\text{H}}{\text{C}}}-$
Poly(vinyl chloride)	PVC	$-\text{CH}_2-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}-$
Poly(ethyl acrylate)	PEA	$-\text{CH}_2-\underset{\text{C}(\text{O})\text{OEt}}{\overset{\text{H}}{\text{C}}}-$
Poly(methyl methacrylate)/Plexiglass	PMMA	$-\text{CH}_2-\underset{\text{C}(\text{O})\text{OMe}}{\overset{\text{CH}_3}{\text{C}}}-$
Poly(tetrafluorethene)/Teflon	PTFE	$-\text{CF}_2\text{CF}_2-$
Poly(butadiene)		$-\text{CH}_2\text{CH}=\text{CHCH}_2-$
Poly(isoprene)	PI	$-\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}=\text{CH}-\text{CH}_2-$
Poly(dimethylsiloxane)	PDMS	$-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{Si}}}-\text{O}-$
Poly(ethylene terephthalate)	PET	$-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-$
Poly(ethylene oxide)/poly(ethylene glycol)	PEO/PEG	$-\text{CH}_2\text{CH}_2\text{O}-$
Poly(lactic acid)	PLA	$-\text{O}-\underset{\text{CH}_3}{\overset{\text{H}}{\text{C}}}-\text{C}(=\text{O})-$

Name	Abbreviation	Repeating unit
Poly(glycolic acid)	PGA	
Poly(vinyl acetate)	PVAc	
Poly(acrylonitrile)	PAN	
Poly(vinyl alcohol)	PVA	
Poly(formaldehyde)		$-\text{CH}_2\text{O}-$
Nylon-6		
Nylon-6,6		
Poly(carbonate)	PC	
Poly(isobutene)		

Remember: Et = CH_3CH_2- , Me = CH_3

Appendix J

Phase rule

The phase rule can be derived quite easily. Suppose we have C compounds, distributed over P phases. How many things can we choose in principle? For each phase, we must specify the pressure, the temperature and the chemical composition. If there is equilibrium, the temperature and pressure are the same for all phases, so this gives only 2 things to specify (p and T). In each phase, we specify the chemical composition as mole fractions (x_i), which must always obey $\sum x_i = 1$. Therefore, we only need $C - 1$ mole fractions to specify the chemical composition of each single phase. For P phases, we therefore need $P(C - 1)$ mole fractions. So we could in principle choose $2 + P(C - 1)$ variables.

However, if there is equilibrium the chemical compositions are not independent in all phases. It can be shown from thermodynamics that each compound has a so-called chemical potential (μ_i), which must be the same in all phases if there is to be equilibrium. For compound i in phases $\alpha, \beta, \gamma, \delta, \dots$ we must therefore have:

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \mu_i^\delta = \dots$$

For P phases, this means that there are $P - 1$ relations that must hold for each component i in all phases $\beta, \gamma, \delta, \dots$:

$$\begin{aligned} \mu_i^\beta &= \mu_i^\alpha \\ \mu_i^\gamma &= \mu_i^\alpha \\ \mu_i^\delta &= \mu_i^\alpha \\ \text{etc. for all remaining phases} \end{aligned}$$

If we do this for all C components, we get $C(P - 1)$ relations that must hold, and that limit the choice of the variables found in the first paragraph.

So we are left with a number of choices that we can freely make: the total number of variables minus the relations necessary for equilibrium. Or, if we call this the degrees of freedom:

$$\mathcal{F} = [2 + P(C - 1)] - C(P - 1) = C + 2 - P$$

This is the phase rule.

Appendix K

Lever rule

The lever rule tells us how to derive the *physical* composition of a two-phase mixture (i.e. how much of the phases is there?) from the *chemical* compositions (i.e. how much of each compound is there in each phase?). How does this work?

Suppose we have m_0 kg of a mixture of compounds A and B. If the average chemical composition of this mixture is x_0 (as mass fraction of A), then there is $m_A = x_0 m_0$ kg of A and $m_B = (1-x_0)m_0$ kg of B.

When this mixture separates into two phases (1 and 2), we get the masses m_1 and m_2 of the phases, with of course $m_1 + m_2 = m_0$. We are now interested in the mass fractions $f_1 = m_1/m_0$ and $f_2 = m_2/m_0$. These describe the *physical* composition. Of course, $f_1 + f_2 = 1$.

Each phase will have its own *chemical* composition: phase 1 will have a mass fraction of A of x_1 , and phase 2 will have a composition x_2 . Then in phase 1 there will be $x_1 m_1$ kg of A, and in phase 2 there will be $x_2 m_2$ kg of A. In total, the amount of A cannot change, so:

$$x_1 m_1 + x_2 m_2 = x_0 m_0$$

When we divide by m_0 , we can also write this as:

$$x_1 f_1 + x_2 f_2 = x_0$$

When we now use the fact that $f_2 = 1 - f_1$, we can isolate f_1 to get:

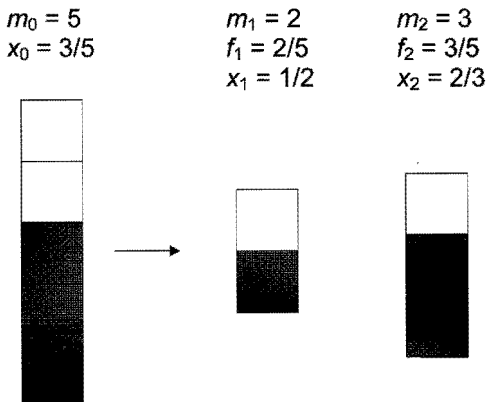
$$f_1 = \frac{x_2 - x_0}{x_2 - x_1}$$

Again using $f_2 = 1 - f_1$, it is now easy to get:

$$f_2 = \frac{x_0 - x_1}{x_2 - x_1}$$

These formulae constitute the lever rule.

If you are lost in all the symbols, perhaps this simple example will help:



Appendix L Packing in ionic solids

When cations (+) and anions (–) are combined into a crystal, their sizes will generally not be the same, and this determines (roughly) the kind of packing or crystal structure you get. We will use the ratio r_+/r_- : since cations are usually smaller than anions, this is in general smaller than 1. We will look what happens when the cation becomes ever smaller. An easy tool is then the coordination number: the number of directly neighbouring ions (N_c).

When $r_+/r_- < 1$, the first situation we get is $N_c = 8$: the so-called cubic arrangement seen in the CsCl structure, where the 8 anions at the corners of a cubic unit cell surround one cation in the centre of the cube (see Figure 4.7). The limit of this situation is reached when the cation becomes so small that the anions start touching along the edges of the cube: when the cation in the centre becomes even smaller, not all 8 anions fit around it anymore, so we switch to $N_c = 6$. We can calculate the radii at which this transition happens: when all the ions touch, we have $a = 2r_-$ for the edge of the cube, and $a\sqrt{3} = 2r_+ + 2r_-$ for the body diagonal (from one corner to the opposite; as for BCC). This yields: $r_+/r_- = \sqrt{3} - 1 = 0.732$. Therefore, we will (roughly) get a CsCl structure for $0.732 < r_+/r_- < 1$.

Not convinced about the $\sqrt{3}$ in the body diagonal? First go diagonally to another corner along the side; then use Pythagoras: when the side is a , the length of the side diagonal is $\sqrt{a^2 + a^2} = a\sqrt{2}$. Then go along the side and do Pythagoras with this side and the side diagonal: this will give you the length of the body diagonal as $\sqrt{\{(a\sqrt{2})^2 + a^2\}} = \sqrt{\{2a^2 + a^2\}} = \sqrt{\{3a^2\}} = a\sqrt{3}$. QED

When $r_+/r_- < 0.732$, we get $N_c = 6$: the octahedral arrangement as seen in the rock salt (NaCl) structure, where the 6 anions in the faces of the cubic unit cell surround a cation in the centre of the cube (see Figure 4.11).

We reach the limit of this arrangement when anions start touching along side diagonals (the same as a “normal” FCC): this is seen clearly in e.g. the bottom plane of the NaCl structure. For smaller cations we switch to $N_c = 4$.

The radii at which this happens follow from the situation where all ions just touch along the side diagonal: we then have $a\sqrt{2} = 4r_-$, and the side of the cubic unit cell here is $a = 2r_+ + 2r_-$. This gives: $r_+/r_- = \sqrt{2} - 1 = 0.414$. Therefore, the NaCl structure will be formed when $0.414 < r_+/r_- < 0.732$.

When $r_+/r_- < 0.414$, we get $N_c = 4$: the tetrahedral arrangement as seen in the zinc blende structure, where anions at the corners and in the faces of the cubic unit cell surround cations inside the cube. The cation is in fact in the centre of a smaller cube with side $a/2$ and 4 anions around it at the corners (Figure 4.10).

Here the limit is reached when the anions start touching along the side diagonal of the cube (as for the one-atom-per-point FCC). Then we have for the side diagonal: $a\sqrt{2} = 2r_-$, and for the body diagonal of the smaller cube: $(a/2)\sqrt{3} = 2r_+ + 2r_-$. This yields: $r_+/r_- = \sqrt{6} - 1 = 0.225$. We will therefore get the zinc blende structure when $0.225 < r_+/r_- < 0.414$.

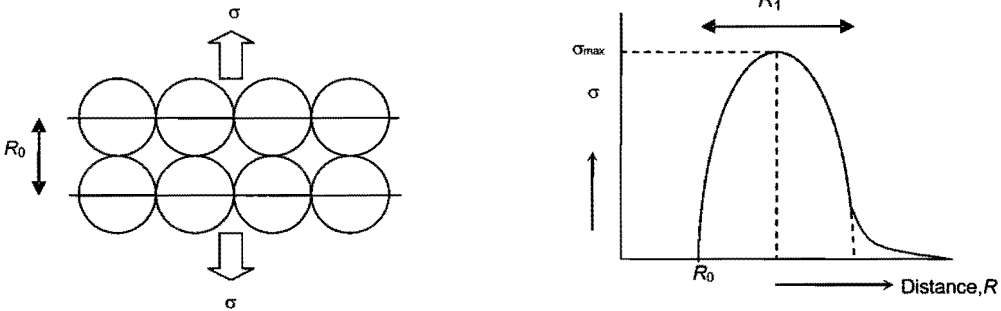
When $r_+/r_- < 0.225$, we get $N_c = 3$ (a triangular arrangement), and for $r_+/r_- < 0.155$ we get $N_c = 2$ (a linear arrangement). We will not look at these cases, as they are not relevant for us.

Appendix M

The Orowan model for brittle fracture

The Orowan model for fracture is a simple model that gives a theoretical (and incorrect) estimate of the tensile stress of a crystalline material.

We assume a perfectly crystalline material, and want to separate two layers of atoms, which are perpendicular to the stress. Normally the atoms are situated at a distance R_0 , and this has to be stretched before the bond can be broken.



We will estimate the maximum stress with a simple model, where the stress first increases to a maximum, and then decreases until the atoms are free of each other.

$$\sigma = \sigma_{\max} \sin \frac{\pi(R - R_0)}{R_1}$$

The stress now has a maximum of σ_{\max} at a distance $R = R_0 + R_1/2$, and fracture is complete at a distance $R = R_0 + R_1$.

In order to determine the maximum stress (or tensile strength), we use the following technique.

For $R \approx R_0$ we can assume elastic behaviour:

$$\sigma = E\varepsilon = E \frac{R - R_0}{R_0}$$

So for the initial slope we can write:

$$\frac{d\sigma}{dR} = \frac{E}{R_0}$$

From the sine-model, we can also calculate the slope:

$$\frac{d\sigma}{dR} = \frac{\sigma_{\max} \pi}{R_1} \cos \frac{\pi(R - R_0)}{R_1}$$

Now, for $R = R_0$ this slope is:

$$\frac{d\sigma}{dR} = \frac{\sigma_{\max} \pi}{R_1}$$

From these two equations for the slope, it follows that the maximum stress is related to an elastic property, viz. Young's modulus:

$$\sigma_{\max} = \frac{ER_1}{\pi R_0} \quad (i)$$

In order to determine the value of R_1 , we have to look at the energy that is necessary to break the bonds on a surface of 1 m^2 . This is given by the integral of the stress, using the sine-model for the stress:

$$\Delta E = \int_{R_0}^{R_0+R_1} \sigma dR = \frac{2\sigma_{\max} R_1}{\pi}$$

This energy must now be equal to the energy necessary to create two new surfaces of 1 m^2 : $\Delta E = 2\gamma$. From these equations it follows that:

$$R_1 = \frac{\pi\gamma}{\sigma_{\max}} \quad (ii)$$

When we combine this with equation (i) that we have derived above, we get for the maximum stress, which is the tensile strength:

$$\sigma_{\max} = \sqrt{\frac{E\gamma}{R_0}}$$

We can also use equations (i) and (ii) to derive a formula for the surface energy:

$$\gamma = \frac{ER_1^2}{\pi^2 R_0}$$

Experimentally we often find that $R_1 \approx R_0$, so $\gamma \approx ER_0/10$, and we then find for the tensile strength:

$$\sigma_T \approx \frac{E}{\pi} \approx \frac{E}{3}$$

Appendix N

The random-coil model in three dimensions

In three dimensions, the random walk model is more complex, since we can move in more directions: every step can be at a different angle to the previous one. We will write the step i as vector \vec{l}_i with length L , so the total walk will be:

$$\vec{R} = \sum \vec{l}_i$$

Now we again use the square, but in this case via the dot product:

$$R^2 = \vec{R} \cdot \vec{R} = (\sum \vec{l}_i) \cdot (\sum \vec{l}_i) = \sum (\vec{l}_i \cdot \vec{l}_i) + 2\sum \vec{l}_i \cdot \vec{l}_j \quad (\text{the last term with } i < j)$$

On averaging over all possible directions, we get:

$$\langle R^2 \rangle = \sum \langle \vec{l}_i \cdot \vec{l}_i \rangle + 2\sum \langle \vec{l}_i \cdot \vec{l}_j \rangle = NL^2 + 2\sum |\vec{l}_i| |\vec{l}_j| \langle \cos \theta \rangle$$

Since $\langle \cos \theta \rangle = 0$ (all values are present both positive and negative in the interval 0 to 2π , or the integral over $(0, 2\pi)$ of $\cos \theta$ is 0), we are again left with:

$$\langle R^2 \rangle = NL^2$$

This can also be seen with a more complicated model: the Gaussian chain. If the polymer chain consists of n_s segments, each with length L_s , then the distribution of the second chain end location (at a distance r_c from the origin) is given by a Gaussian distribution:

$$W(x, y, z) = \frac{b_s^3}{\pi^{3/2}} e^{-b_s^2 r_c^2} \quad [\text{m}^{-3}]$$

with:

$$b_s = \sqrt{\frac{3}{2n_s L_s^2}} \quad [\text{m}^{-1}]$$

The chance to find the second chain end at a distance r_c in any possible direction, so on a spherical surface of radius r_c , is then given by:

$$W(r_c) = 4\pi r_c^2 W(x, y, z) \quad [\text{m}^{-1}]$$

The end-to-end distance r_c will of course be different for different polymer chains, and at different times. In order to give an average size of the randomly coiled polymer chain, one usually works with the root-mean-square value of the end-to-end distance r_c . This average can also be compared easily to experimental results. It can be shown that this average value is:

$$\langle r_c^2 \rangle = \int_0^\infty r_c^2 W(r_c) dr_c = n_s L_s^2 \quad [\text{m}^2]$$

Appendix O Answers to Problems

2.1.a. 2.0011 m

b. 3.6 m

2.2. $\varepsilon = 0.004$

2.3.a. $\Delta L = 0.31$ mm

b. $\Delta d = -0.0092$ mm

2.4.a. 5.8 km

b. ~~ε_{max}~~ = 0.00217; top $\varepsilon_{\text{Y,max}} = 0,00219$

c. bottom

2.5.a. $E = 138$ GPa

b. $\sigma_{\text{Y}} = 345$ MPa

c. $\sigma_{\text{T}} = 1034.5$ MPa

d. 0.43 MJ/m³

e. 110.8 MJ/m³

f. 15%

2.6.a. $E = 170$ GPa

b. $\sigma_{\text{T}} = 410$ MPa

c. 85 kJ/m³ (for $\varepsilon_{\text{Y}} = 0.001$)

d. 18.3%

2.7.a. $E = 353$ GPa

b. $\sigma_{\text{T}} = 1250$ MPa

c. 46%

d. $\sigma_{\text{t}} = 1650$ MPa (via: $\sigma_{\text{t}} = \sigma(1 + \varepsilon)$) or $\sigma_{\text{t}} = 2040$ MPa (via: $\sigma_{\text{t}} = \sigma A_0/A$)

2.8.a. $\varepsilon_{\text{t}} = 0.3$

b. $\varepsilon = 0.35$

c. $\sigma_{\text{t}} = 913$ MPa, $\sigma = 676$ MPa

2.9.a. $\varepsilon_{\text{t}} = 0.237$

b. $\varepsilon_{\text{t}} = 0.20$: $\varepsilon = 0.22$, $\sigma = 471.3$ MPa; $\varepsilon_{\text{t}} = 0.237$: $\varepsilon = 0.267$, $\sigma = 473.6$ MPa

2.11.a. $d_0 = 1.99$ mm

b. $F = 1766$ N

3.1.a. $R_0 = (2B/A)^{1/6}$

b. $B/A = 1.22 \times 10^{-58}$ m⁶

c. $U(R_0) = -A/(2R_0^6)$

3.2.a. LiF (690 GPa)

b. LiF: -0.57 MJ/mol; NaBr: -0.41 MJ/mol

- 3.3.a. both 0.86×10^{-11} N, but with different signs
 b. compression: -1.1 nN; tension: $+0.68$ nN

- 3.4.a. $U_0 = D(1 - R_0/\rho)\exp(-R_0/\rho)$
 b. $U_0 = (\rho/R_0 - 1)(C/R_0)$

3.5. $n = \text{~~0.25~~ } 1.25$

- 4.1.a. 0.2633 nm
 b. 0.1798 nm

- 4.2.a. FCC with 1 atom/point
 b. BCC with 1 atom/point

4.3. $6.62 \times 10^{-29} \text{ m}^3$

4.4. $6.04 \times 10^{28} \text{ atoms/m}^3$

4.5. 3.7%

4.6. 3.45%

4.7. 1.85 Mg/m^3

4.8. 3.37 Mg/m^3 ; 8 atoms per cell

- 4.9.a. 4 each
 b. FCC

4.10. 1: $[\bar{1}41]$; 2: $[121]$; 3: $[1\bar{2}0]$

4.11. a: $(\bar{2}12)$; b: (014) ; c: (101)

4.12. f, h, and i

4.13.a. (113)

b. x-axis: $(3,0,0)$; y-axis: $(0,3,0)$; z-axis: $(0,0,1)$

c. $[1\bar{1}0]$ or $[\bar{1}10]$

4.14. $\rho = 2.34 \text{ Mg/m}^3$

4.15.a. $r = 0.125$ nm

b. 2 atoms/cell

4.16. Any vector with $h + 4k + 2l = 0$

5.1. 28 kN

5.2.a. 0.73 mJ

b. 94.1 J

- 5.3.a. $\gamma_{LS} = 0.66 \text{ J/m}^2$
b. $W_{c,Hg} = 0.94 \text{ J/m}^2$, $W_{c,glass} = 0.60 \text{ J/m}^2$
c. $W_a = 0.11 \text{ J/m}^2$, $S = -0.83 \text{ J/m}^2$

- 5.4.a. 500 MPa
b. 2.2 mm

5.5. 1.8 mm

5.6. $\sigma^* = 16.2 \text{ MPa}$

5.7. Fracture occurs

- 5.8.a. $\rho = 0.4 \text{ nm}$
b. $\sigma^* = 1.48 \text{ GPa}$

- 5.9.a. $\sigma^* = 590 \text{ MPa}$
b. $\gamma = 360 \text{ J/m}^2$

- 5.10.a. $\sigma = 567.7 \text{ MPa}$
b. $\varepsilon_Y = 0.0015$

5.11. 11.7%

5.12. [120]

6.2. DP = 1240

6.3. 45.6 kg/mol

6.4. DP = 330

- 6.5.a. Isoprene: 0.443; butadiene: 0.557
b. 5.31 g

6.6. $M_n = 24.15 \text{ kg/mol}$; $M_w = 24.68 \text{ kg/mol}$

- 6.7.a. $M_n = 33.04 \text{ kg/mol}$
b. $M_w = 36.24 \text{ kg/mol}$
c. 786.7
d. 862.9
e. $D = 1.097$

- 6.8.a. 0.802
b. 0.420
c. Worse packing

6.9. 0.091

- 6.10.a. Smaller side groups: more flexible polymer chain
b. Smaller side groups: more flexible polymer chain
c. Dipolar interactions and H-bonds: less flexible
d. Double substitution: less flexible
- 6.11. $\langle r_c^2 \rangle^{1/2} = 3.4 \text{ nm}$; $R_g = 1.39 \text{ nm}$
- 6.12. 3.05 mol
- 7.1.a. Crystallinity
b. Crosslinks
c. Temperature
d. Crosslink number
- 7.2. 83.3 days
- 7.3.a. $\eta = 6.06 \times 10^{11} \text{ Pa}\cdot\text{s}$
b. $\varepsilon = 0.01$
- 7.4.a. $\tau_R/\tau_K = 0.25$
c. $\tau_K = 0.2 \text{ s}$; $\tau_R = 0.05 \text{ s}$; $\tan(\delta) = 0.6, 0.75, 0.69$ at 5, 10, 15 rad/s, respectively.
- 7.5. $\lambda = 1.5$: $\sigma = 0.53 \text{ MPa}$; $\lambda = 0.8$: $\sigma = -0.38 \text{ MPa}$
- 7.6. $c^* = 0.61 \text{ mm}$
- 7.7. $a = 55 \mu\text{m}$
- 7.8. $\sigma_T = 44 \text{ MPa}$
- 7.9.a. $w = 1.5 \text{ MJ/m}^3$
- 8.1. $r_0 = 10.43 \text{ mm}$
- 8.2. Cold-work to 36 %CW: $d = 12.8 \text{ mm}$; anneal; cold-work to 22 %CW.
- 8.3. 2.87 mm to 0.34 mm
- 8.4. $d = 0.0147 \text{ mm}$
- 8.5.a. 4750 g
b. ca. 64 wt% sugar
- 8.6.b. ca. 6.5 wt% salt

- 8.7.a. 94 mol% Sn, 6 mol% Pb
- b. $\mathcal{F} = 2$: above 220 °C; $\mathcal{F} = 1$: between 220 and 183 °C; $\mathcal{F} = 0$: exactly at 183 °C; $\mathcal{F} = 1$: below 183 °C
- c. 90 wt% Sn: β -particles in layered eutectic matrix; 10 wt% Sn: β -particles in α -matrix
- 8.8. 2800 °C: only L, $x_L = 50$ wt% Re;
 2452 °C: L + β , $x_L = 43$ wt% Re, $x_\beta = 56$ wt% Re, 46 wt% L, 54 wt% β ;
 2448 °C: α + β , $x_\alpha = 48$ wt% Re, $x_\beta = 56$ wt% Re, 75 wt% α , 25 wt% β ;
 1000 °C: α + β , $x_\alpha = 40$ wt% Re, $x_\beta = 59$ wt% Re, 47 wt% α , 53 wt% β
- 8.9.a. Just below 1147 °C: γ + Fe₃C, $x_\gamma = 2.14$ wt% C, $x_{\text{Fe}_3\text{C}} = 6.67$ wt% C, 70 wt% γ , 30 wt% Fe₃C;
 900 °C: γ + Fe₃C, $x_\gamma = 1.27$ wt% C, $x_{\text{Fe}_3\text{C}} = 6.67$ wt% C, 59 wt% γ , 41 wt% Fe₃C; just below 727 °C: α + Fe₃C, $x_\alpha = 0.022$ wt% C, $x_{\text{Fe}_3\text{C}} = 6.67$ wt% C, 48 wt% α , 52 wt% Fe₃C
- 8.10. 36.3 s
- 9.1.a. 32 GPa
 b. 4.4 GPa
- 9.2. 7%
- 9.3. $E_m = 3.15$ GPa; $E_f = 72.1$ GPa
- 9.4. 33.3 MPa
- 9.5.a. 0.125 mm
 b. $V_f = 0.799$
 c. $W_f = 62.4$ kJ/m²
 d. $E_c = 61.3$ GPa
 e. $K_{1C} = 87.5$ MPa·m^{1/2}
- 9.6.a. $\sigma_T = 10.8$ MPa
 b. $E_1 = 2.1$ MPa; $E_2 = 34.6$ MPa
 d. 1.73 MJ/m³
- 9.7.a. Isostrain: $V_f = 0.31$; isostress: $V_f = 0.48$
 b. $\tau_{fm} = 19.2$ MPa

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