IB - Materials

2023-2024

Thermodynamics of Materials

Lecturer: Prof Alexandre Kabla

How to use the handouts

The squared numbers (2) on the right margin of the handouts indicate the slide number on the presentation. In case you get lost... 2

> This is the style used to highlight mathematical/technical parts of derivations. Don't worry if it looks daunting at first, this is just a bit of algebra without new physical concepts introduced. You may want to work on these on your own time and make sure you understand the steps. Although the content is part of the course and examinable, expect a bit of guidance if we ask you to recapitulate it.

There are also sections of the handouts titled "To go further". These sections extend slightly the content, providing links to other courses or sometimes full derivations. This is not examinable material.

Online Resource 1: Additional material on Moodle

The Moodle page of the course is:

`https://www.vle.cam.ac.uk/course/view.php?id=70121`

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1 Introduction

IA Materials

In the IA materials course, several important aspects of materials engineering were introduced: 3

1. Defining and measuring materials properties:
   - stiffness, strength, toughness, ductility, friction, visco-elasticity.
2. Microstructural basis of material properties:
   - Stiffness: crystal structure, atomic bonding, inter-atomic forces
   - Strength of metals: dislocations, yield, plasticity
   - Polymers: molecular structure, glass transition
3. Designing with materials:
   - Material selection: performance indices, stiffness limited design, strength limited, influence of shape on material optimisation,
   - Elasticity analysis: stresses and strains in elastic materials, linear visco-elasticity framework,
   - Introduction to manufacturing processes (casting, rolling, forging).

IB Materials

In the IB course, we will further study how material microstructure influences material properties, and how processing techniques can control microstructure. 4

1. Defining and measuring materials properties:
   - Plasticity, creep and material failure
2. Microstructural basis of material properties:
   - Polymer elasticity
   - Phase equilibrium and transformation
   - Diffusion
3. Designing ~~with~~ materials:
   - Practical processes for manipulating microstructure and properties (e.g. casting and heat treatment of metals, polymer processing)
   - Modelling deformation and failure
   - Protecting materials from corrosion

What questions will we ask and answer?

Given these general aims, we need to gain a deeper understanding of certain physical concepts. The course will primarily focus on two types of questions: 5

- **Thermodynamics**. Could a transformation happen? What is the equilibrium state?
- **Kinetics**. If the transformation can happen, what is its rate?

Particular examples are:

- Consider a material made of several components. Would they mix or phase separate? Why, and how quickly would it happen? How can we fine tune the microstructure of the material?
- Consider a metal in a given environment, would it be chemically attacked, and how quickly would it happen? What protective measures could we take?

Microstructural basis of material properties

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- We care about large scale, macroscopic properties, but we usually control composition and to some extent microstructure. How do we link the two? This is the job of Thermodynamics.
- You are familiar already with Classical Thermodynamics, which combines elegantly a mathematical framework, robust principles, and an empirical characterisation of materials to link the different state variables, such as the ideal gas law.
- In our case, we need to grasp the origin of these otherwise empirical relationships. This builds on assumptions regarding the microscopic worlds, and a lot of statistics to derive what an observer at large scale would perceive.
- But what are we averaging on at the microscale? What are the properties that matter? How do we average?
- We will learn how to tackle such problems, in a very simplified way (by picking the simplest possible systems) and use it to derive material properties and qualitatively understand some important aspects of materials processing.

Lecture plan

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- **A. Microstructure and entropy**

  We will discuss how entropy accounts for the microscopic scale.

  We will characterise the entropy of mixing of two components in solution.

  We will study two materials whose mechanical properties are controlled by entropy: ideal gases, and flexible polymers.

- **B. Driving forces in material transformations**

  How to predict the evolution of a system operating at constant pressure and temperature? We will adapt the second law of thermodynamics to study phase equilibrium, transformations and osmotic pressure.

- **C. Particle diffusion**

  We will study diffusion, an important microscopic mechanism controlling the rate of many processes.

  We will investigate the case of Si doping in semiconductors.

- **D. Application of thermodynamics and diffusion to corrosion**

  We will introduce basic principles of electrochemistry and apply them to study corrosion, oxide formation and protective methods.

The approaches introduced in this section are particularly relevant to the following courses: IB Thermofluids, 3A5 (Thermo and power generation), 3C1 (Materials processing and design), 3G2 (Mathematical physiology), 3G5 (Biomaterials), 3F7 (Information Theory and Coding), 3M1 (Mathematical Methods, 4A9 (Molecular thermodynamics), 4G1 (Mathematical biology of the cell), 4G5 (Molecular Modelling).

2 Entropy and Materials

2.1 Revision

First law - conservation of energy

The internal energy U is the total kinetic and potential energy of all the microscopic constituents of a material. 8

The variation of internal energy of a system that receives a heat energy Q from its environment and produces a work W is:

$$\Delta U = Q - W$$
$$dU = \delta Q - \delta W$$

If the work is due to pressure forces only:

$$\delta W = pdV \implies dU + pdV = \delta Q$$

where p is the pressure and V the volume.

Second law - irreversible processes

In Classical Thermodynamics, entropy is a thermodynamic property whose variation from a state 1 to a state 2 is defined by: 9

$$S_2 - S_1 = \int_1^2 \left(\frac{dQ}{T}\right)_{rev}$$

In combination with Clausius theorem, it sets limits to the range of transformations that are physically possible.

$$dS = \frac{\delta Q}{T} + \delta S_{irr} \text{ with } \delta S_{irr} \geqslant 0$$

This has deep implications regarding the spontaneous evolution of a system. For instance, the entropy of an isolated system where $\delta Q = 0$ must increase, and be maximum at equilibrium.

Most irreversible processes can be related to entropy. 10

- Particle diffusion makes a system evolve towards the most likely microscopic configurations,
- Diffusing particles carry their kinetic energy; this leads to heat transfer.
- Diffusing particles carry their momentum; this leads to viscosity.

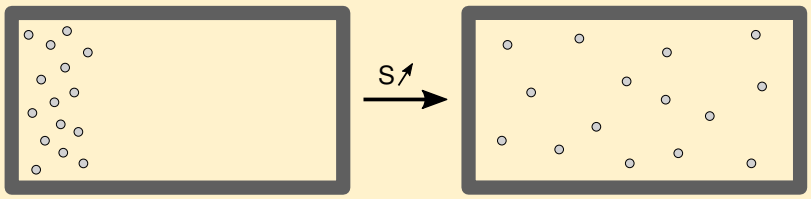

Figure 1: Diffusion occurs in such a way that it increases entropy.

2.2 Microscopic states and definition of Entropy

Macro-states and micro-states

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- You are already familiar with the concept of macro-state of a system from classical thermodynamics. This is the set of properties such as temperature, pressure and volume that together determine the thermodynamic state of the system.
- A micro-state relates to the state of the material at the smallest relevant length scale. It would mean for us a record of the positions, orientation, velocities and angular velocities of all the particles/molecules involved. This represents a lot of information!
- For a given macro-state, there exist many compatible microstates.

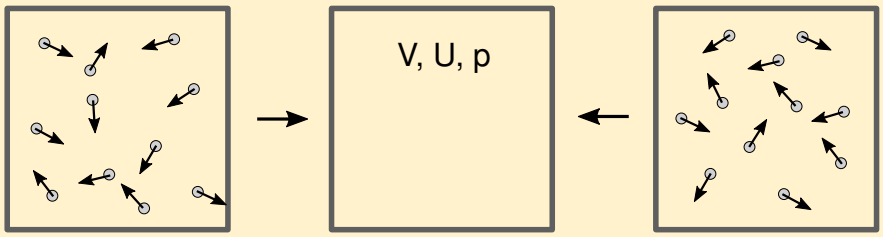

Figure 2: One macrostate corresponds to many microstates.

Entropy: a measure of uncertainty regarding the micro-state

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- Entropy captures the uncertainty regarding the microstate, given the macro-state.
- The number Ω of microstates for a given macro-state is a measure of this uncertainty.
- How many micro-states exist for particles of internal energy U in a isolated box of volume V?

Number of microstates

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- One would think with reason that there is an infinite number of microstates corresponding to a given macrostate.
- In practice, we will need to worry about how that number changes with the macro-state variables, not about the details.
- However, quantum mechanics and the principle of uncertainty provide a physical justification for estimating a finite number.

Number of microscopic configurations

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- In this section, we will focus on systems at set temperature that change geometry.
- The distribution of velocities will be assumed to be constant, but the distribution of positions will change.
- Therefore, we will focus on the number of microscopic configurations, a subset of the total state that is easier to grasp.
- We will also discretise space and angles to facilitate counting, and will show that results will remain robust nonetheless.

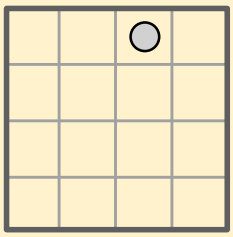

Figure 3: To facilitate counting, microscopic configurations can be discretised.

The microscopic definition of Entropy

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- We aim to quantify entropy in terms of the number of microstates Ω, as a measure of uncertainty about the microstate.
- However, Ω doesn't match our expectations for an Entropy from a classical perspective. In particular, it is not extensive:
- Consider two systems, each containing Ω_1 and Ω_2 microstates, the total number of states is not the sum $\Omega_1 + \Omega_2$, but the product $\Omega_1 \cdot \Omega_2$.

- Taking the log of Ω solves this issue and provides a very powerful link between micro-state statistics and classical thermodynamics.

$$S = k_B \ln \Omega$$

k_B is the Boltzmann Constant:

$$k_B = 1.380649 \times 10^{-23} \text{J K}^{-1}$$

Note that this is not a proof, but rather an attempt to give you insight into this very peculiar relationship that links the microscopic and macroscopic worlds.

Entropy: links with Information Engineering

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- The link between Entropy and uncertainty is very profound and has many applications beyond Thermodynamics.
- From an Information perspective, one can revisit the example of the particle in the box, and ask how many Yes-No questions we should ask, at a minimum, to know where the particle is.
- This number, expressed in bits, represents the information content of this answer, or the uncertainty of not knowing it. It is also called Entropy by analogy with statistical thermodynamics.

2.3 Entropy of mixing

In this section, we are going to consider a first example of how entropy can be related to the composition and microstructure of a material. This example will become particularly relevant when we start interpreting phase diagrams later in the course.

Entropy of a mixture

Consider two components A and B, with n_a atoms of A and n_b atoms of B that are allowed to mix. What is the change of entropy of the system associated with the mixing of A and B? 17

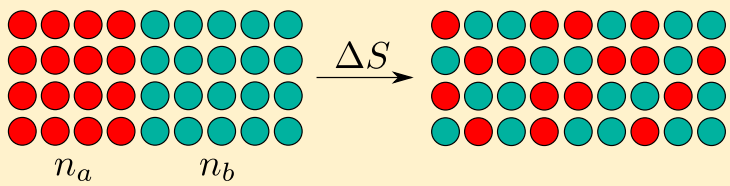

Figure 4:

The number of microstates (based on spatial arrangements only) is of the order of $\Omega = C_{n_a}^{n}$ with $n = n_a + n_b$.

The change of entropy is:

$$\Delta S = k_B \ln(\Omega) = k_B \ln\left(\frac{n!}{n_a! n_b!}\right)$$

This expression is nice, but it is challenging our understanding of thermodynamics. For instance, S should be an extensive property, i.e. its value should be proportional to n keeping the proportion of A and B constant. This requirement is not obvious at this point.

Thermodynamic limit

There is a useful approximation of $n!$ in the limit of large values of n, where classical thermodynamics is valid. This formula is in the Maths databook. 18

Stirling approximation: for n large, $\ln n! \approx n \ln n - n$.

$$\ln \Omega = n \ln n - n - (n_a \ln n_a - n_a + n_b \ln n_b - n_b) = n \ln n - n_a \ln n_a - n_b \ln n_b$$

$$\ln \Omega = n_a \ln n + n_b \ln n - n_a \ln n_a - n_b \ln n_b = -n_a \ln x_a - n_b \ln x_b$$

where $x_a = n_a/n$ and $x_b = n_b/n$ represent the composition of the material.

$$\Delta S = -k_B \left(n_a \ln x_a + n_b \ln x_b\right) = -n\, k_B \left(x_a \ln x_a + x_b \ln x_b\right) \tag{1}$$

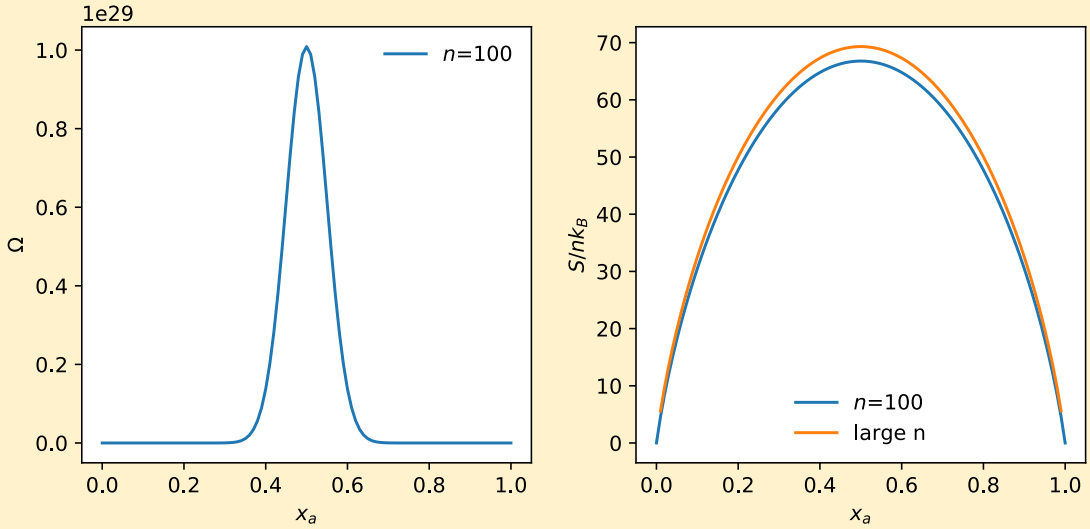

Figure 5: Left: Number of microstates as a function of the proportion of A. Right: Entropy (per molecule) for a given number n of particles, and in the limit of large n values.

It is now apparent that, in the limit of large n, i.e. in the thermodynamic limit, the entropy of mixing is extensive, proportional to n and function of the composition of the material (x_a, x_b).

We said earlier in the revision section that the entropy of an isolated system must increase. We see here that the mixing entropy is necessarily positive, i.e. mixing would tend to happen spontaneously, which makes sense if we think about the diffusion process of atoms or molecules. But this argument is incorrect in general without considering (i) how a system interacts with its environment, how much heat and work are exchanged as mixing occurs, and (ii) how the different components interact with each other once mixed - think about oil and water for instance. As we will see later in the course, the Gibbs free energy G encapsulates all these contributions. But for now, let's investigate further how entropy and microstructure/geometry are related, and how these relationship can control the mechanical properties of certain materials.

Summary

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- The microscopic definition of entropy $S = k_B \ln \Omega$ allows us to calculate changes in entropy associated with microstructural transformations.
- The mixing of two components strongly increases entropy by creating many more configurations the system can explore.
- The mixing entropy is extensive in the limit of large systems, aka the thermodynamic limit.

2.4 Ideal gases and entropy

What is an ideal gas?

Gases at low density all exhibit similar thermodynamical properties and obey the Ideal Gas Law 20

$$pV = NRT$$

In this regime, molecules are all far away from each other and seldom interact. Their potential of interaction is largely irrelevant.

Our proposition here is that the Ideal Gas Law reflects the dominant role of entropy in the materials behaviour. Let's investigate!

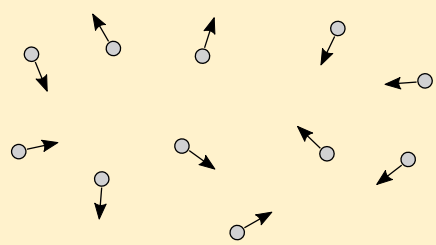

Figure 6: Ideal gases have a low density so that particle interactions can be neglected.

Internal energy of an ideal gas

The internal energy U of an ideal gas only involves the kinetic energy of the molecules and is largely independent of the nature of gas. 21

$$U = \Sigma_i \frac{1}{2} m_i v_i^2 \quad (+\text{rotational kinetic energy})$$

The internal energy is therefore a function of temperature only:

$$U = U(T)$$

Based on this property of the system and some basic thermodynamic principles, we can establish the Ideal Gas Law.

Ideal gas in a piston

Consider an ideal gas in a piston kept at constant temperature T. 22

For an infinitesimal change in volume dV, the First Law of thermodynamics tell us that:

$$dU = \delta Q - \delta W$$

For a reversible transformation, $\delta Q = TdS$ and $\delta W = pdV$. This leads to the "TdS" equation you have seen in IA:

$$TdS = dU + pdV$$

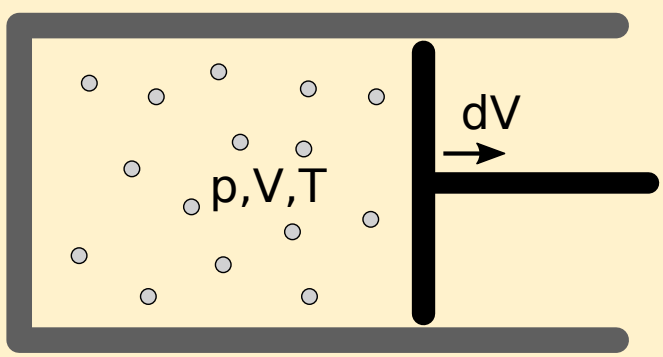

Figure 7: Gas trapped in a piston at temperature T.

Because the gas is ideal, we know that a change in volume dV alone would not change the internal energy. Hence:

$$TdS = pdV \tag{2}$$

To establish a state equation, we therefore need to get an expression for $\frac{\partial S}{\partial V}$.

Entropy of an ideal gas

The entropy S is *a priori* a function of U (or T) and V. To find an expression for S, we need to go beyond classical thermodynamics and use the microscopic interpretation of entropy introduced at the end of the IA course. 23

$$S = k_B \ln \Omega$$

where k_B is the Boltzmann constant and Ω the number of microstates, i.e. number of ways to set the positions and velocities of the molecules in a volume V and with an internal energy U, assuming an isolated system.

In the context of a system in contact with a thermostat, the expression is more complex due to the fact that the internal energy of the microstates fluctuate around the thermodynamic mean U. The statistics is in general complex to extract, and requires careful analysis.

In an ideal gas, because the particles do not interact with each other, the way to distribute the velocities is independent of the way to distribute positions. The number of microstates Ω is the product of a term accounting for the possible ways to distribute velocities Ω_v and the number of ways to distribute positions Ω_c

Ω_v only depends on the range of velocities that molecules can take. Hence it depends on the T, but not V. By contrast, the number of configurations Ω_c only depends on the volume available V, and not the temperature T.

$$\Omega = \Omega_v(T) \cdot \Omega_c(V)$$

Therefore, we have:

$$S = k_B \ln \left(\Omega_v(T) \cdot \Omega_c(V)\right)$$

$$S = k_B \ln \left(\Omega_v(T)\right) + k_B \ln \left(\Omega_c(V)\right)$$

$$\frac{\partial \mathbf{S}}{\partial \mathbf{V}} = \mathbf{k_B} \frac{\partial (\ln \mathbf{\Omega_c})}{\partial \mathbf{V}} = \mathbf{k_B} \frac{\mathbf{1}}{\mathbf{\Omega_c}} \frac{\partial \mathbf{\Omega_c}}{\partial \mathbf{V}} \tag{3}$$

Numbers of configurations Ω_c

From equation 3, it is clear that any multiplicative factor in the expression of Ω_c will cancel out. We therefore just need to know how Ω_c scales with V. 24

- The number of ways to place a particle in the volume V is proportional to the volume.
- Since the particle density is very low, we can ignore the fact that particles limit the space available to the others.
- Hence, the number of ways to place a second particle having placed the first one is again proportional to V, and so on.

If we have n particles, the number of ways to place them in the volume will therefore take the form:

$$\Omega_c = \mathbf{KV^n} \tag{4}$$

where K is a numerical constant.

Ideal gas law

Substituting equation 4 into equation 3, we get: 25

$$\frac{\partial S}{\partial V} = k_B \frac{1}{KV^n} KnV^{n-1} = \frac{k_B n}{V} \tag{5}$$

Combining now with equ. 2, we get:

$$\frac{p}{T} = \frac{\partial S}{\partial V} = \frac{k_B n}{V}$$

Which leads to the ideal gas law:

$$pV = nk_B T$$

If we consider N moles of gas, we get:

$$pV = NRT$$

with $N = n/\mathcal{N}_A$, $R = k_B \mathcal{N}_A$, and $\mathcal{N}_A$ is the Avogadro number.

This shows that the pressure of gas in the ideal limit is purely entropic. This is why all gases tend to have the same behaviour at low density, regardless of the nature of their molecules.

To go further: links with your Thermofluids course

In IB Thermofluids (first lecture of the fluid dynamics section, starting around week 6), an expression for the pressure on an interface is derived based on transfer of linear momentum every time a molecules bounces against it.

$$p = \frac{n}{V} m \langle v_x^2 \rangle$$

where m is the mass of individual molecules. This can be combined with the ideal gas law derived above ($pV = nk_BT$) to determine the relationship between mean velocity and temperature:

$$\frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} k_B T$$

The total kinetic energy of a mono-atomic gas, e.g. He is:

$$\frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m \left(\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle \right) = \frac{3}{2} k_B T$$

The internal energy of a mole of gas is $\frac{3}{2}RT$. From this, one can deduce important information about the heat capacity of gases. For instance, for a monoatomic gas, it would be $C_V = \frac{3}{2}R$.

Summary

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- The Ideal Gas Law reflects the entropic nature of diluted gases.
- It can be derived by combining classical thermodynamics with the microscopic definition of entropy $S = k_B \ln \Omega$.
- This is a first example of how to use (statistical) thermodynamics to derive mechanical properties of materials.
- The Gas Constant R is simply the Boltzmann constant k_B when amounts of material are expressed in moles: $R = \mathcal{N}_A k_B$

This example illustrates in a simple case how to use the microscopic definition of Entropy to derive material properties. We will now use the same approach to study polymer mechanics and apply the result to understand the elastic behaviour of rubber.

3 Elasticity of compliant materials

3.1 Stiffness of polymers

Soft matter

A large number of common materials are soft (low yield stress) and/or compliant (low stiffness) at room temperature. Examples are: 27

- Elastomers and gels,
- Suspensions of colloids[1], pastes,
- Emulsions[2] (Ex: milk or mayonnaise)
- Most biological materials.

This class of materials is called "*Soft Matter*".

Engineering applications

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- Rubber is an important engineering material. It is a unique natural material with high flexibility and excellent grip properties. Synthetic elastomers share similar properties. Key applications are tires, o-rings, timing belts, rubber bands, gloves, etc.
- The texture of a food or cosmetic product is an essential part of consumer experience, and often effectiveness.
- In the growing industry of tissue engineering and regenerative medicine, a common approach is to build a polymer scaffold on which cells will proliferate and differentiate in the right kind of cells. The biochemical and mechanical properties of the scaffold are key to successfully develop a functional tissue.

[1] fine Brownian particles too small to sediment

[2] An emulsion is a foam like material made of micron size droplets of a fluid A in a non-miscible fluid B.

Natural rubber

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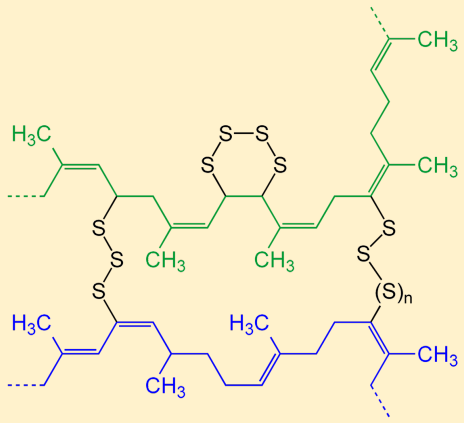

Figure 8: Schematic structure of crosslinked chains of natural rubber after vulcanisation. Source: Wikimedia

- Natural rubber (caoutchouc) is produced from latex, harvested from hevea trees.
- Latex needs to be cured to become rubber. The curing process of rubber is called **vulcanisation** . It is done by adding a few per cent of sulphur to the polymers, and heating the mixture at about 170°C for 10-15 mins.

Online Resource 2: Rubber manufacturing

Extraction of natural rubber
How It's Made, Discovery channel

https://www.vle.cam.ac.uk/mod/url/view.php?id=5388201

Rubber band manufacture
How It's Made, Discovery channel

https://www.vle.cam.ac.uk/mod/url/view.php?id=5388211

Some solids are stiff, others compliant. Why?

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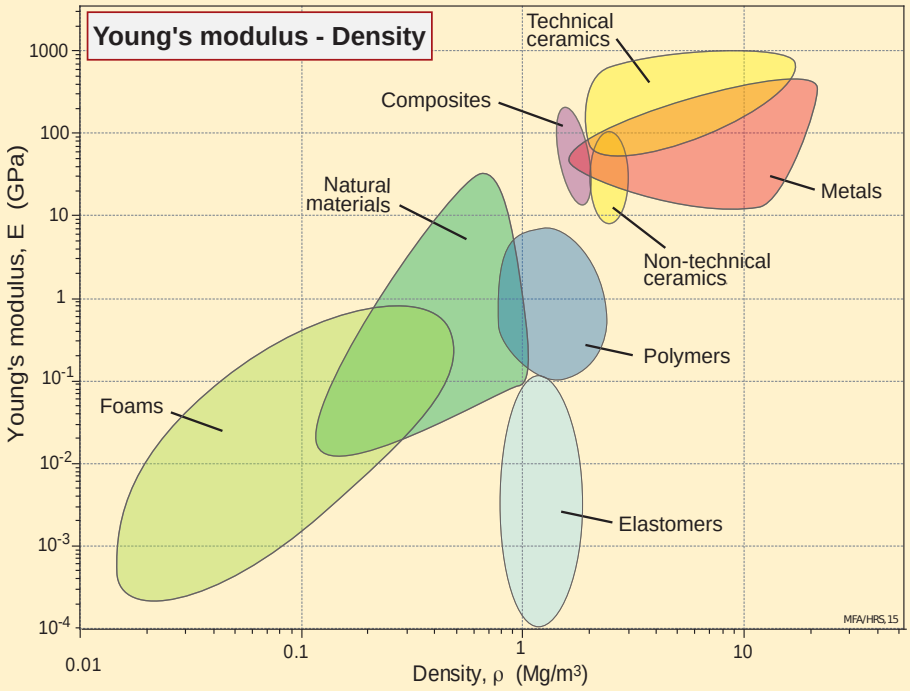

Figure 9: Plot of Young's modulus vs density for a range of materials. After Ashby, Shercliff, Cebon, 2013. Materials: Engineering, Science, Processing and Design, Butterworth-Heinemann

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- Metals, ionic crystals (ex: salt) or covalent solids (diamond) commonly have Young's moduli in the range of 10-1000 GPa. Their stiffness is determined by the atomic potential of interaction. Electrostatic interactions are responsible for attractive forces between atoms or molecules. Steric (contact) interactions cause short range repulsion. The balance between the two sets atomic distances and the rigidity of these bonds.

- Foams have a large fraction of air trapped, forming cells within the material. These materials are light and easy to deform because deformations are accommodated by bending the cell walls, with greatly reduced distortion at the atomic scale. Many natural materials, such as wood or bone, also have cellular structures.

Polymers

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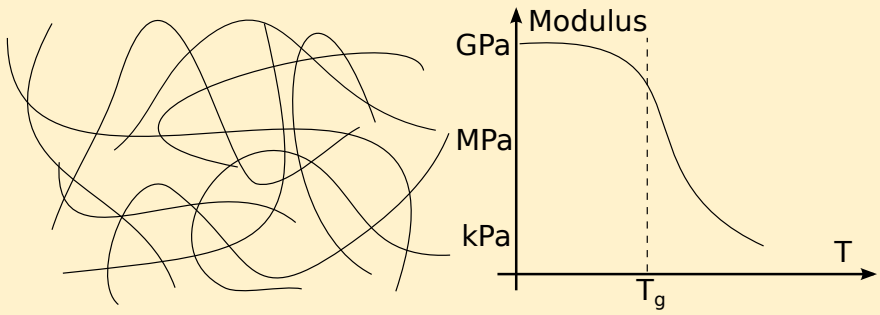

Figure 10: Structure of linear polymers (amorphous) and their mechanical properties.

Polymers have very different behaviours below and above their glass transition temperature T_g.

- Below, the thermal energy is too weak to allow the chains to slide past each other. The stiffness therefore relates to the rigidity of the polymer chains, typically of the order of GPa.
- Above the glass transition, polymers are **viscoelastic** . In this regime, the chain is flexible and fluctuates due to thermal agitation. On short time scales, polymer chains are entangled and can store deformation, leading to a transient elastic response. Under steady load, polymers are however liquid and flow above T_g.

Elastomers

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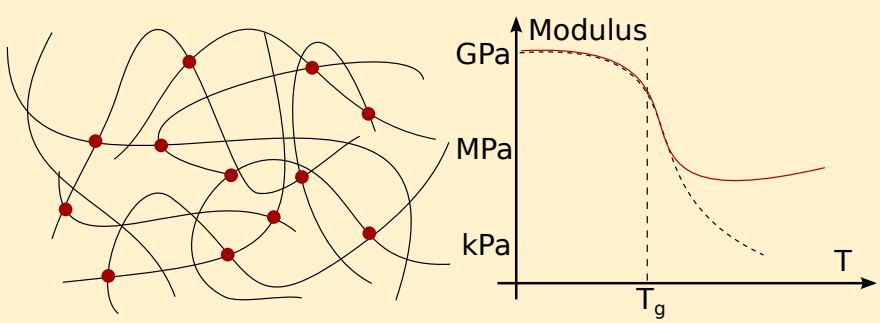

Figure 11: Structure of cross-linked polymers (amorphous) and their mechanical properties.

Elastomers are **crosslinked networks** of polymer chains. **Rubber** is one of them. These materials also experience a glass transition associated with a significant drop in the Young modulus, but remain solid above T_g.

Above T_g, we have a network of “liquid” polymer chains, which raises a number of important questions:

- Why is this network elastic?
- What aspect of the microstructure controls the elastic modulus of the rubber above T_g.

The concept of *microscopic entropy* is important to answer these questions.

3.2 Polymer chains

Stretching a single polymer chain

Consider a floppy polymer chain made of n monomers of length a, and contour length $L = na$. 34

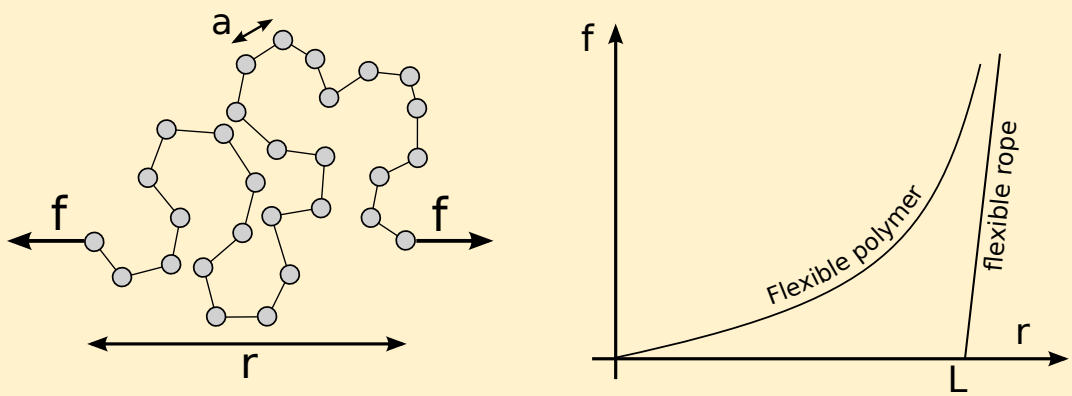

Figure 12: Structure of linear polymers (amorphous) and their mechanical properties.

We will now derive the relevant thermodynamic equations that will allow us to study the role of Entropy in the response of a single chain.

Thermodynamics of a polymer chain under tension

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- The polymer is maintained at constant temperature T.
- For any small change in the system, the First Law of Thermodynamics gives:

$$dU = \delta Q - \delta W$$

- For a reversible transformation, $\delta Q = TdS$ and $\delta W = -fdr$, where f is the tension in the chain. This leads to a new form of the "TdS" equation:

$$TdS = dU - fdr \tag{6}$$

To find the force, we need to estimate dU and TdS for a given change of the end-to-end distance dr.

Internal energy U of the polymer chain

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- The internal energy U depends on temperature and bond stretching.
- If the chain is fully flexible, U should not change when the conformation of the polymer is changed by bending the chain.
- As long as $r \ll L$, U does not depend on r.

This leads to:

$$f = -T\frac{\partial S}{\partial r} \tag{7}$$

Configurational entropy of the polymer chain

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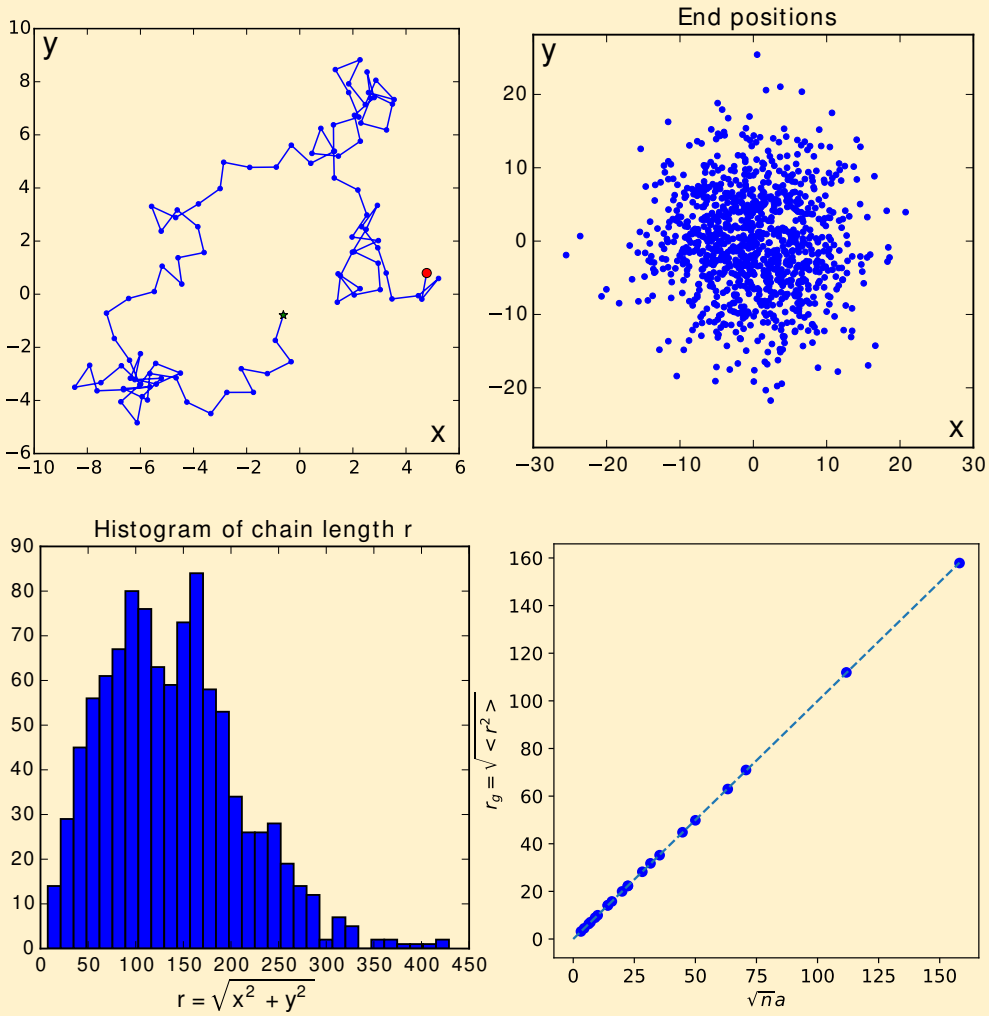
- We need to calculate $\frac{\partial S}{\partial r}$.
- As with ideal gases, since we work at constant temperature, the relevant part of the entropy is due to accessible configurations: $S = k_B \ln \Omega_c$.
- The question is: if the end-to-end distance of a polymer chain is r, how many different configurations could the chain have? And how does this number vary with r?
- The statiscal problem we are dealing with is an example of a random walk, or drunkard's walk, commonly found in statistics. We will use it twice in this course.

Online Resource 3: 2D Polymer chain configurations

Simulating the 2D statistics of polymer configurations with ramdom walks
iPython Notebook

https://www.vle.cam.ac.uk/mod/url/view.php?id=16195871



Configurations of a 1D polymer chain

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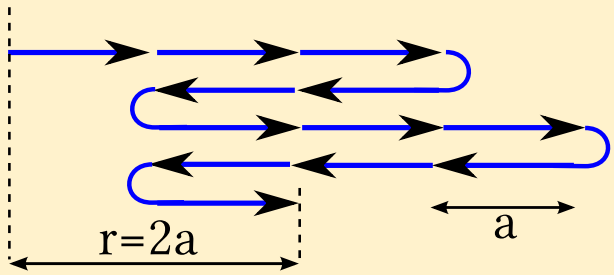

Figure 13: 1D model of a polymer

- Consider a 1D chain of length L and number of monomers n. Results can be generalised to 2D and 3D - see online iPython Notebook.
- Monomers all have a length a and are oriented either towards the "$+$" direction, or the "$-$" direction.

If the chain has n_+ and n_- monomers in the “+" and “-" orientations respectively, the end-to-end distance r is therefore:

$$r = n_+ a - n_- a$$

It does not matter in which order the “+" and “-" segments are arranged. The number of suitable configurations therefore is:

$$\Omega_c = C_{n_+}^n = \frac{n!}{n_+! n_-!} \tag{8}$$

We now need to express this quantity as a function of r.
We have:

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$$\begin{cases} n_+ a - n_- a & = r \\ n_+ + n_- & = n \end{cases}$$

Inverting these expressions to get n_+ and n_-, we get:

$$\begin{cases} n_+ & = \frac{1}{2}\left(n + \frac{r}{a}\right) \\ n_- & = \frac{1}{2}\left(n - \frac{r}{a}\right) \end{cases} \tag{9}$$

Equation 8 then becomes:

$$\Omega_c = \frac{n!}{\left(\frac{1}{2}\left(n + \frac{r}{a}\right)\right)! \left(\frac{1}{2}\left(n - \frac{r}{a}\right)\right)!} \tag{10}$$

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The Stirling approximation can be used to simplify these expressions:
For n large, $\ln n! \approx n \ln n - n$.
Using this relationship in Equations 10:

$$\ln \Omega_c = n \ln n - \frac{1}{2}\left(n + \frac{r}{a}\right) \ln\left(\frac{1}{2}\left(n + \frac{r}{a}\right)\right) - \frac{1}{2}\left(n - \frac{r}{a}\right) \ln\left(\frac{1}{2}\left(n - \frac{r}{a}\right)\right) \quad (11)$$

$$\ln \Omega_c = n \ln n - \frac{1}{2}\left(n + \frac{r}{a}\right) \ln\left(n + \frac{r}{a}\right) - \frac{1}{2}\left(n - \frac{r}{a}\right) \ln\left(n - \frac{r}{a}\right) + n \ln 2 \quad (12)$$

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Consider the function $f(x) = x \ln x$.

$$\ln \Omega_c = f(n) - \frac{1}{2} f\left(n + \frac{r}{a}\right) - \frac{1}{2} f\left(n - \frac{r}{a}\right) + n \ln 2 \quad (13)$$

This can be simplified further using Taylor series:

$$f(x + dx) = f(x) + dx f'(x) + \frac{dx^2}{2} f''(x) + O(dx^3)$$

$$f(x) - \frac{1}{2} f(x + dx) - \frac{1}{2} f(x - dx) = 2\frac{1}{2}\frac{dx^2}{2} f''(x) = -\frac{dx^2}{2}\frac{1}{x} + O(dx^3)$$

Back to 13 with $x = n$ and $dx = \frac{r}{a}$ in the limit where $r/a \ll n$:

$$\ln \Omega_c \approx -\frac{r^2}{2na^2} + n \ln 2 \quad (14)$$

Configurational entropy of the polymer chain

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- We want to calculate $f = -T\frac{\partial S}{\partial r}$.
- Since $S = k_B \ln \Omega_c$ and $\ln \Omega_c \approx -\frac{r^2}{2na^2} + n \ln 2$, we have:

$$f = \frac{k_B T}{na^2} r \quad (15)$$

- The entropic spring constant of a polymer chain is therefore $\frac{k_B T}{na^2}$. This result remains valid in 3D.

Typical length of a polymer chain

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- In the absence of any force, the mean end-to-end vector is $\underline{0}$, as illustrated by the previous equation, and as required by symmetry - there is no reason for the polymer to go to the right more than the left in the absence of any force.
- But, the mean end-to-end distance is not zero. Let's calculate $\sqrt{< r^2 >}$, also called radius of gyration, r_g.

  Using again equation 14:

$$\ln \Omega_c \approx -\frac{r^2}{2na^2} + n \ln 2 \implies \Omega_c \propto \exp\left(-\frac{r^2}{2na^2}\right)$$

Ω_c is proportional to the probability to get a chain with end-to-end positions separated by r. The end-to-end positions are therefore normally distributed, with mean 0 (as explained above) and standard deviation $\sigma^2 = na^2$. The radius of gyration is the standard deviation of the distribution in this simple model. In 2D or 3D, a similar result would be obtained (see numerical analysis in Online Resource 2).

$$r_g = \sqrt{< r^2 >} \approx \sqrt{n}a \tag{16}$$

To go further: fluctuation energy of a spring

We saw that the kinetic energy in an ideal gas was such that $\frac{1}{2}k_bT$ was stored in each direction of movement. Is there a similar relationship for the polymers?

The energy stored in a spring is $E = \frac{1}{2}kr^2$ where r is the extension and k the spring constant, which is, in our case, $k = \frac{k_BT}{na^2}$.

Due to thermal fluctuations, we have seen that the mean extension (or end-to-end distance) for a flexible polymer is $r_g = \sqrt{n}a$.

We therefore have: $E = \frac{1}{2}kr_g^2$ which becomes, after substituting the expressions for r_g and k:

$$E = \frac{1}{2}kr_g^2 = \frac{1}{2}k_BT$$

We can therefore interpret the role of entropy as equivalent to storing $\frac{1}{2}k_bT$ in the polymer spring.

Summary

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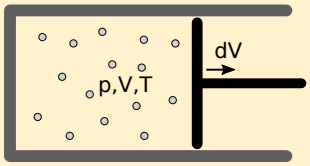
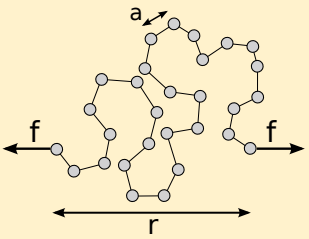
- The elasticity of flexible polymer chains is due to entropy. The larger the end-to-end distance, the lower the number of available microscopic configurations.
- A flexible polymer with n monomers each of size a has the following properties:
  - its mean end-to-end distance (radius of gyration) is $r_g = \sqrt{n}a$,
  - its effective spring constant is: $k_B T/na^2 = k_B T/r_g^2$.

Analogy between flexible polymers and ideal gases

		
Thermo	$TdS = dU + pdV$	$TdS = dU - fdr$
Perturbation	dV	dr
Assumptions	T constant $dU = 0$ (ideal gas)	T constant $dU = 0$ (flexible chain)
Equilibrium	$\frac{\partial S}{\partial V} = \frac{p}{T}$	$\frac{\partial S}{\partial r} = -\frac{f}{T}$
Microstate number	$\Omega_c \propto V^n$	$\Omega_c = \frac{n!}{\left(\frac{1}{2}\left(n+\frac{r}{a}\right)\right)!\left(\frac{1}{2}\left(n-\frac{r}{a}\right)\right)!}$
State equation	$pV = nk_B T$	$f = \frac{k_B T}{na^2} r$

3.3 Rubber mechanics

Cross-linking structure of an elastomer

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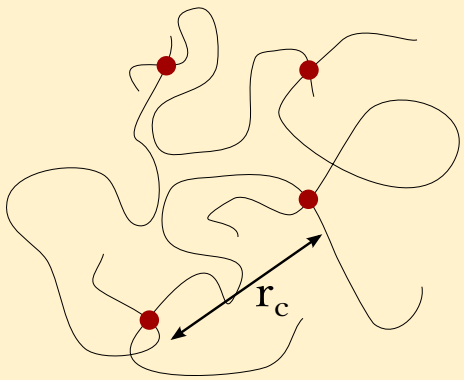

Figure 14: Sketch of a polymer network. r_c is the average distance between crosslinks on a polymer chain.

Rubber and other elastomers are **dense crosslinked networks** of flexible polymers in a liquid state. This essentially links all the polymers into a single giant molecule.

Between crosslinks, we have established that a chain behaves like a spring. It is therefore useful to consider the mean distance between crosslinks along a chain, r_c and how these springs are connected to each other.

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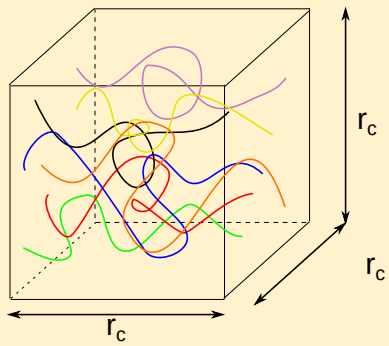

Figure 15: Polymers in a volume element of size r_c x r_c x r_c.

In a cube of material of dimension r_c x r_c x r_c, all the sections of polymers between crosslinks are primarily acting in parallel, rather than in series. So we can use this volume element to estimate the modulus more easily.

To estimate the elastic modulus of the elastomer from the results of the previous section, we need to find:

- the effective stiffness of the polymer segments that connect the crosslinks,
- the density of such segments in the bulk material.

Polymer structure between cross-links

To know the stiffness of a polymer segment connecting two crosslinks, we need to know the number of monomers between the two cross-links(see equation 15). 47

When cross-linking takes place, polymers are just behaving like single flexible polymers in the absence of tension. According to equation 16, the typical distance between two points in the chain separated by n monomers is $\sqrt{n}a$.

Hence, the number n_c of monomers between cross-links is given by:

$$r_c = \sqrt{n_c}a \implies n_c = \frac{r_c^2}{a^2} \tag{17}$$

The effective spring constant of each polymer segment between cross-links is therefore:

$$k = \frac{k_B T}{n_c a^2} = \frac{k_B T}{r_c^2} \tag{18}$$

Density of polymer segments

We have many of these chains in the bulk of the elastomer. We now need to find the density of the chain segments, i.e. how many segments per unit volume. 48

Let's calculate the number N_c of chain segments in a cube of volume r_c^3.

$$N_c = \frac{\text{number of monomers in } r_c^3}{\text{number of monomers per chain}}$$

$$N_c = \frac{r_c^3/v_m}{n_c} = \frac{a^2 r_c}{v_m} \tag{19}$$

where v_m is the volume of a monomer.

Modulus of the elastomer

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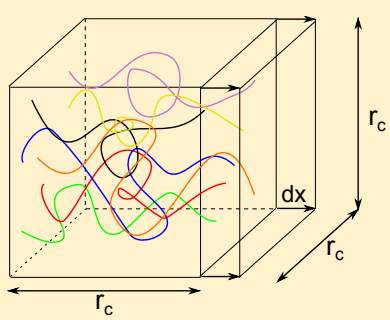

Figure 16: Extension of a volume element of size r_c x r_c x r_c.

Considering again a cube of volume r_c^3. The force F if the cube is stretched by a distance δx is:

$$F = N_c k \delta x = \frac{a^2 r_c}{v_m} \cdot \frac{k_B T}{r_c^2} \cdot \delta x = \frac{k_B T a^2}{v_m r_c} \delta x$$

$$\sigma = \frac{F}{r_c^2} \text{ and } \epsilon = \frac{\delta x}{r_c} \implies E = \frac{\sigma}{\epsilon} = \frac{F}{\delta x \; r_c}$$

This leads to (using equ. 17):

$$E = \frac{\mathbf{k_B T a^2}}{\mathbf{v_m r_c^2}} = \frac{\mathbf{k_B T}}{\mathbf{v_m n_c}} \tag{20}$$

This relationship is one of the hallmarks of elastomers' elasticity: their stiffness increases with temperature. This is visible experimentally, but it is often limited due to the proximity to the glass transition of the polymers which tends to cause a decrease of the apparent stiffness with temperature.

Natural rubber

For natural rubber crosslinked with 2-3 per cent of sulphur, n_c would be of the order of 200-300. The volume of a monomer of the flexible chain would be of the order of $v_m \approx 10^{-28}$m^3 (source: Tabor, *Gases, Liquids and Solids*, chapter 13). At room temperature, this leads to $E \approx 10^5$Pa, which is a bit low, but in the right range of values. 50

Summary

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- The elastic modulus of an elastomer above the glass transition can be estimated by:

$$E = \frac{k_B T}{v_m n_c}$$

  where v_m is the volume of a monomer and n_c the number of monomers between cross-links.

- Increasing the amount of crosslinkers is an effective way to control the elastic modulus of the elastomer.

Conclusion

This section of the course demonstrates how a physical understanding of materials helps us identify the primary parameters controlling their mechanical properties, adjust the manufacturing and processing of materials to obtain the desired characteristic, such as the elastic modulus, and evaluate the range of realistic values for these characteristics. In the context of rubber, we now appreciate why they exhibit such a low modulus given their density; they are not solids like metals or ceramics, but crosslinked liquids driven by the thermal fluctuations of polymers. The important parameters are the polymer/monomer characteristics and crosslinking density. There is a lot more to explore for a complete picture. We only focused here on small deformations, but the material can stretch a lot and the relevant physics becomes more subtle. Rubber is also a viscoelastic material, and its response depends on the deformation rate, as introduced in the IA course.

Intended Learning Outcomes

The intended learning outcomes of this section are:

- Explain the distinction between the macroscopic and the microscopic states of a system.
- Explain the significance of the microscopic definition of entropy.
- Apply this definition to derive approximate expressions for the entropy of simple systems: mixing entropy, ideal gas (spatial configurations only for given volume), ideal polymers for given end-to-end distance.
- Analyse numerically the statistics of ideal polymers, as an example of random walk, and identify the parameters controlling their configuration statistics (in particular the radius of gyration as a function of the number of monomers).
- Apply classical thermodynamics and the definition of the microscopic entropy to extract the ideal gas law and entropic spring constant of an ideal polymer. Explain the key assumptions and limitations.
- Explain qualitatively the link between the single polymer analysis and the elastic modulus of rubber, with a particular focus on cross linker density and temperature.

You can test yourself against these to make sure you have covered the relevant content, and return to your notes if necessary. The week 1 quiz and examples paper questions may now be fully attempted and will also cover most of these learning outcomes.