3. Polymers

Polymers and polymer solutions form a huge and important class of soft condensed matter.

Polymers may be:

synthetic

- polystyrene
- polyethylene
- other plastics, artifical fibres and glues

of biological origin,

- rubber
- starch
- proteins
- nucleic acids (e.g. DNA)

Polymers often are major components in complex *composite materials*, both natural and artificial:

- Glass reinforced plastic (glass fibre)
- Wood
- Tissue

Despite the very wide variety of different properties of polymers that arise from the different chemistry that makes them up, many of their physical properties have *universal* characteristics: these characteristics are a result of *generic* properties of long, string like, molecules. An example of such a generic property is the fact that two molecules can't cross one another this leads to the effect of *entanglement*, which produces dramatic viscoelastic effects in polymer melts and solutions. Surprisingly, it proves possible to construct remarkably simple and general theories to account for these properties.

3.1 The variety of polymeric materials:

Variety in physical state

Polymers are found in a variety of different physical states:

Liquid

Polymer melts and solutions are liquids - but they are often very viscous and show marked viscoelastic properties

Crystalline

Polymers can crystallise, but usually crystallisation is not complete.

Familiar materials like *polyethylene* are usually semi-crystalline.

Liquid crystalline

Some polymers are rather rigid molecules, which can line up to form liquid crystalline materials. These can form the basis of very strong engineering material, like *Kevlar*. The molecular orientation thus obtained can lead to useful optoelectronic properties in semi-conducting polymers like *poly fluorene*.

Glasses

Because polymers often find it difficult to crystallise, polymer glasses are very common. *Polystyrene* and *Poly (methyl methacrylate) (Perspex)* are common examples.

Chemistry



Stereochemistry

Stereochemistry is important for chains with more than one type of group attached to the main chain carbons. For example, in polypropylene X=H and $Y=CH_3$.

Isotactic



Atactic



Atactic chains possess *quenched disorder* - there is an entropy contribution that will be present even at absolute zero.

Atactic chains find it difficult or impossible to crystallise.

Architecture

Chains can be *linear* (e.g. high density polyethylene, proteins):



or branched (e.g. low density polyethylene, amylopectin (a component of starch)



or part of a network (e.g. rubber, epoxy resin)



Copolymers

Normal polymers (homopolymers) are composed of a single molecular repeat unit:

AAAAAAAAAAAA

One can have polymers made up of different types of repeat unit - these are called *copolymers*. Different arrangements are possible:

Random copolymers

Repeat units are arranged at random along the chain. Properties often are intermediate between the properties of the two homopolymers:

ABBABABBBAAABABABB

Block copolymers

Here the molecule is made up of different blocks containing only a single monoment:

triblock AAAAAAABBBBBBBBBBBBBAAAAAAAAAA

These molecules can *self-organise* into complex structures, in which the different monomer types *microphase separate*.

Sequenced copolymers

Proteins and DNA form a special class of polymer in which a variety of different monomer types are arranged in a particular, well defined but not repeating, sequence. This results in the ability of a single molecule to self-organise into a complex three dimensional structure.

3.1 The random walk and the dimensions of polymer chains

What is the mean end to end distance of a polymer chain?

The simplest model is the **freely jointed chain:**

We assume the chain to be made up of N links, each of length a; the different links have **independent** orientations.

The end to end vector is the vector sum of the N jump vectors which represent the direction and size of each link.

$$\mathbf{r} = \mathbf{a}_1 + \mathbf{a}_2 + \ldots + \mathbf{a}_N = \sum_{i=1}^{N} \mathbf{a}_i$$

The mean end to end distance is

$$\langle \mathbf{r} \cdot \mathbf{r} \rangle = \left\langle \left(\sum_{i=1}^{N} \mathbf{a}_{i} \right) \cdot \left(\sum_{j=1}^{N} \mathbf{a}_{j} \right) \right\rangle$$

Expanding the sum gives us

$$\langle \mathbf{r}^2 \rangle = \sum_i \sum_j \mathbf{a}_i \cdot \mathbf{a}_j$$

Thus
$$\langle \mathbf{r}^2 \rangle = \mathbf{N}\mathbf{a}^2 + \sum_{i \neq j} \langle \mathbf{a}_i \cdot \mathbf{a}_j \rangle$$

If the chain is freely jointed the directions of different links are completely uncorrelated and we get the familiar random walk result

$$\langle \mathbf{r}^2 \rangle = \mathbf{N}a^2$$

The overall size of a random walk is proportional to the *square root* of the number of steps.

Real polymer chains - short range correlations

This seems terribly unphysical as a model for a polymer chain; elementary chemistry tells us that successive links along a polymer chain have definite bond angles. Thus the cross terms do not disappear; neighbouring vectors are correlated.

Consider a model in which the bond angle is fixed at q, but is free to



rotate:

now $\langle \mathbf{r}_i \cdot \mathbf{r}_{i-1} \rangle = a^2 \cos \theta$, and in general $\langle \mathbf{r}_i \cdot \mathbf{r}_{i-m} \rangle = a^2 \cos^m \theta$.

Thus the correlation dies away along the chain. This means we can conceive of breaking the chain up into subunits, whose size we choose to be **larger** than the range of the correlations.



Now, suppose there are g links per subunit, whose vectors are \mathbf{c}_i , we can write

$$\langle \mathbf{r}^2
angle = \frac{N}{g} \langle \mathbf{c}^2
angle = Nb^2$$

where b is an effective monomer size, the **statistical step length**. In practise the effect of correlations along the chain is often characterised in terms of the **characteristic ratio** C_{∞} :

$$C_{\infty} = \frac{b^2}{a^2}.$$

If you know the chemical details of your polymer the characteristic ratio may be calculated; alternatively one can extract its value for a given polymer from experimental data on chain dimensions.

This simple example is typical of the way in which polymer physics tries to proceed: the long range structure (in this case the scaling of chain dimensions with the square root of the degree of polymerisation N) is given by statistics and is **universal** - i.e. independent of the chemical details of the polymer in question. All these chemical details go into one parameter, which may either be calculated on the basis of detailed theory at the atomic level, or extracted from experiment.

Excluded volume

In the argument above for the mean end to end distance of a polymer we accounted for interactions between **neighbouring** links of the chain, but we neglected interactions between **distant** points on the chain. It turns out that for an isolated chain these interactions are important, and affect the long range structure of the chain.

At the simplest level, we know that the chain cannot intersect itself; the monomer units have finite volume and two cannot be in the same place at the same time. We have a **self-avoiding walk**. The mathematics of SAW's is much more complicated than for simple random walks; instead of finding $\langle \mathbf{r}^2 \rangle^{\frac{1}{2}} = a N^{\frac{1}{2}}$, the random walk result, we find $\langle \mathbf{r}^2 \rangle^{\frac{1}{2}} = a N^{\frac{\nu}{2}}$, where the exponent n > 0.5. The effect of excluded volume, then, is to swell the polymer chain over the random walk value.

What is the value of the exponent n? An simple mean-field argument due to Flory gives a value of 3/5. This is amazingly close to the actual value, which can be computed using complicated renormalisation group techniques and is (to three decimal places) 0.588.

Experimentally, the chain dimensions of very dilute chains in good solvents are found to be swollen in the way predicted (though available experimental precision is not really able to distinguish between the Flory value of 3/5 and the more exact value).

Chain statistics in polymer melts - the Flory theorem

In dilute solution, polymers do not follow random walk statistics - because of excluded volume interactions, the chain is swollen.

What happens as we make the solution more complicated, ultimately arriving at the polymer melt? Counterintuitively, rather than becoming more complicated, things become more simple: in the melt chains follow ideal random walk statistics!

This was first realised in 1949 by Flory and put on a sound theoretical footing by Edwards in 1966, when he introduced the idea of **screening**. Here is a simple plausibility argument.

Consider schematic plots of the segment concentration across a section through space; for a dilute solution chains are isolated and segments do not interact with segments from different chains:



distance

The effect of the excluded volume interaction is to include an unfavourable energy proportional to the probability of two segments being close together; that is proportional to c^2 . This leads to a force on the segments proportional to $c\frac{dc}{dx}$, which tends to make the chain expand. Now as the concentration is increased chains start to overlap; $\frac{dc}{dx}$ is smaller and the repulsive force is reduced.







distance

Thus there is **no** repulsive force between the segments and the chain follows ideal random walk statistics. This result was confirmed by neutron scattering in the early seventies.

Measuring the size of polymer chains

The dimensions of polymer chains are most directly measured by *scattering*.

This method relies on the interference of waves scattered from different parts of an extended scattering object.



At large angles, waves scattered from different parts of the object interfere destructively.

The way the intensity drops off with angle depends on the relative magnitude of the inverse size of the object and the *scattering vector* q, which is related to the wavelength of the wave λ and the angle through which it is scattered θ :

 $q = 4 \pi \sin(\theta) / \lambda$.

The size of the object is characterised by the radius of gyration R_{a}

Formally the radius of gyration is defined as the mean squared distance of each point on the object from its centre of gravity. For a random walk it can be shown that $R_g^2 = \langle R_{end-to-end}^2 \rangle / 6$.

How do we decide what type of radiation to use? The two factors that are important are:

• wavelength

the radiation must have a wavelength comparable to the inverse size of the object, so that we can detect scattering from the object.

• contrast

the radiation interacts differently with the object than with the medium it is immersed in.

The types of radiation used are

• light:

contrast based on refractive index differences long wavelength means that large objects scatter to wide angles

• x-rays

contrast based on differences in electron density smaller wavelength means that large objects scatter to smaller angles

• neutrons

contrast based on differences in nuclear interactions scattering very different for hydrogen and deuterium smaller wavelength means that large objects scatter to smaller angles

Although neutron scattering is expensive, the fact that it can distinguish between hydrogen and deuterium means that it can measure chain dimensions in concentrated solutions and melts - this cannot be done any other way.



Dilute solution of polymers - light, x-ray or neutron scattering can be used to determine chain dimensions.



Concentrated polymer solution or melt - scattering experiments cannot pick out an individual polymer chain, and thus cannot measure the overall chain dimensions.



One chain has been *labelled* with deuterium - a neutron scattering experiment can now measure the chain dimensions of an individual molecule in a melt or concentrated solution

Elasticity of a single polymer chain

For a simple random walk (i.e. the freely jointed chain model of a polymer) we derived the mean squared end-to-end distance as $\langle \mathbf{r}^2 \rangle = Na^2$

We can also derive the distribution of possible end-to-end distances, by relatively straightforward statistical mechanics. The result is that the probability distribution function $P(\mathbf{r},N)$ that gives the probability that a chain with N links which has one end at the origin has its other end at position \mathbf{r} is given by

$$P(\mathbf{r},N) \propto \exp\left(-\frac{3\mathbf{r}^2}{2Na^2}\right).$$

We can use this to write down the **configurational entropy** of a polymer as a function of its elongation:

$$S(\mathbf{r}) = -\frac{3}{2} \frac{k_B \mathbf{r}^2}{Na^2} + \text{constant}.$$

When a polymer is stretched, its entropy is lowered. This results in an **increase** in the free energy:

$$F(\mathbf{r}) = \frac{3}{2} \frac{k_B T \mathbf{r}^2}{Na^2} + \text{constant}.$$

A polymer chain behaves like a spring; if it is stretched beyond its ideal random walk size there is a restoring force proportional to the extension. This force is entirely **entropic** in origin.

3.2 Rubber elasticity

The first statistical mechanical theory of the mechanical properties of a polymeric material was the classical theory of rubber elasticity.

A **rubber** is a polymer melt in which crosslinks, randomly placed between adjacent chains, covalently bond the chains together to form a macroscopic network. At a local level, the material behaves like a liquid; in particular the bulk modulus is rather high and to a first approximation the material may be taken as incompressible. However the crosslinks mean that macroscopic bulk flow cannot take place, and the material has a finite shear modulus. The classic theory of rubber elasticity uses statistical mechanics to calculate the shear modulus.



Schematic drawing of a rubber: "x" marks a crosslink, joining strands of polymer of average number of monomer units N_x . The length of each monomer unit is a.

To calculate the modulus, we start by making an important assumption: that when the rubber is deformed each individual crosslink point moves in proportion to the deformation of the whole sample. This is the assumption of **affine deformation**.



Consider a single strand between two crosslink points; take the origin at one crosslink and the second crosslink at x,y,z.

The mean end to end distance of the strand when the rubber is undeformed is given by the random walk formula:

$$r_o^2 = x^2 + y^2 + z^2 = Na^2$$

After deformation we have

$$\mathbf{r}_1^2 = \lambda_x^2 \mathbf{x}^2 + \lambda_y^2 \mathbf{y}^2 + \lambda_z^2 \mathbf{z}^2$$

As we saw above, the entropy of a random walk with mean squared end to end distance r is given by:

$$\mathbf{S}(\mathbf{r}) = -\frac{3}{2}\mathbf{k}\frac{\mathbf{r}^2}{\mathbf{Na}^2}$$

Thus the change of entropy of a strand on deformation is

$$\Delta S_{\text{strand}} = \frac{-3k}{2Na^2} \Big[(\lambda_x^2 - 1)x^2 + (\lambda_y^2 - 1)y^2 + (\lambda_z^2 - 1)z^2 \Big]$$

If there are n strands per unit volume, and using the relation

$$\langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = \frac{1}{3} Na^2$$

we can write the total entropy change per unit volume as

$$\Delta \mathbf{S}_{\text{total}} = -\frac{\mathbf{nk}}{2} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3).$$

Now the simplest type of deformation is simple elongation in the x direction, for which

PHY 369 /02 - Soft Condensed Matter - R.A.L. Jones

section 3 p20

$$\lambda_{\mathrm{x}} = \lambda, \quad \lambda_{\mathrm{y}} = \lambda_{\mathrm{z}} = \frac{1}{\sqrt{\lambda}},$$

where we have used the fact that rubber is incompressible. Thus we can write the entropy change as

$$\Delta S_{\text{total}} = -\frac{nk}{2}(\lambda^2 + \frac{2}{\lambda} - 3).$$

Associated with this change in entropy is a change in free energy given by $F(\lambda) = \frac{nkT}{2} \left[\lambda^2 + \frac{2}{\lambda} - 3 \right].$

We can now obtain the relation between stress t and strain e by noting that l=1+e, and $t=\frac{dF}{de}$; thus $\tau = nkT \left[(1+e) - \frac{1}{(1+e)^2} \right].$

This is a non-Hookian stress/strain behaviour (see the graph below), but we can expand for small strain to find that the Young modulus is E=3nkT. Once again assuming incompressibility (and thus a Poisson's ratio of 0.5) this gives for the shear modulus G

G=nkT.

Another convenient way to express this results, that we will use later, is in terms of M_X , the average molecular weight between crosslinks, and the density r:

 $G{=}\frac{rRT}{M_X} \ .$



Stress strain relationship for rubber, showing both experimental behaviour (points) and the prediction of simple theory.

3.3 Viscoelasticity in polymers and the reptation model

Viscoelasticity: the phenomenology

What is the difference between solids and liquids? We expect solids to behave elastically, with Hooke's law relating shear stress and shear strain: $\sigma = G e$.

For liquids, however, it is the **shear strain rate** that is related to the shear stress, via the viscosity h:

 $\sigma = \eta \frac{de}{dt}$

Thus we distinguish between two types of behaviour. Solids behave elastically; a deformation stores energy in the form of strain energy, and when the stress is relaxed the bodies original shape is recovered. On the other hand liquids flow irreversibly, losing all memory of their original shape, and losing energy in dissipative processes.

In fact all materials can show both types of behaviour, depending on the **timescale** of the measurement; a material has a **relaxation time** τ , such that measurements on a time scale shorter than t produce elastic behaviour, and measurements on a long time scale show viscous behaviour.

Small molecule liquids have very small values of τ (perhaps 10⁻¹¹ s or so) and so behave for most purposes in a completely viscous way, while crystalline materials such as metals may have relaxation times that may be many years (recall the earlier section of the course about creep behaviour). Some materials, however, have relaxation times of order seconds, and it is these that are normally thought of as viscoelastic. Examples of such materials are polymer melts, polymer solutions, and suspensions and other concentrated colloidal dispersions.

Creep Compliance

Apply a constant stress at t=0, and look at the strain as a function of time:



If the applied stress is s0, then the strain as a function of time t is given by $e(t) = \sigma_0 J(t)$

where J(t) is the **creep compliance**

Stress relaxation

Apply a fixed strain e_0 , and watch the stress decay with time:



 $\mathbf{s}(t) = \mathbf{e}_0 \mathbf{G}(t)$

G(t) is the **stress relaxation modulus**

Oscillatory deformations

If an oscillatory shear strain of the form

 $e(t) = e_0 \cos \omega t$

is applied then the stress is given by

 $\sigma(t) = e_0 [G'(\omega) \cos(\omega t) - G''(\omega) \sin(\omega t)]$

where $G^*(\omega) = G'(\omega) + iG''(\omega)$ is called the **complex modulus**. This is related to the stress relaxation modulus through a Fourier transform:

$$G^*(\omega) = i\omega \int_0^{\infty} e^{-i\omega t} G(t) dt.$$

Thus G^{*} can be divided into:

in phase component G' - the **storage modulus**; the elastic component of the response;

out of phase component G'' - the **loss modulus**; the viscous component of the response.

The phase angle of the response is usually called $\boldsymbol{\delta}$, given by $\tan \boldsymbol{\delta} = \mathbf{G}''_{\mathbf{G}'}$

Linear viscoleasticity and the Boltzmann superposition principle

For small deformations we can assume that each loading step makes and independent contribution to the total loading history, and the final deformation is simply the sum of the response to each step:



Thus we can write:

$$\mathbf{e}(t) = \int_{-\infty}^{t} \mathbf{J}(t-\tau) d\sigma(t) = \int_{-\infty}^{t} \mathbf{J}(t-\tau) \frac{d\sigma(t)}{d\tau} d\tau$$

Likewise:

$$\sigma(t) = \int_{-\infty}^{t} G(t-\tau) \frac{\mathrm{d}e(t)}{\mathrm{d}\tau} \mathrm{d}\tau.$$

If we have a steady shear rate this recovers Newton's law of viscosity (i.e. if $\frac{de(t)}{d\tau} = e = constant$);

 $\sigma(t) = \eta_0$ where $\eta_0 = \int_0^\infty G(t - \tau) d\tau$; here η_0 is the **zero shear viscosity**.

PHY 369 /02 - Soft Condensed Matter - R.A.L. Jones

section 3 p27

Time Temperature superposition

It is found experimentally that curves of viscoelastic quantities as a function of <u>time</u> (or frequency) at different <u>temperatures</u> may be superposed onto a single curve using a quasi-universal <u>shift factor</u> aT:

$$\log(a_{\rm T}) = \frac{-C_1^{\rm g}({\rm T} - {\rm T}_{\rm g})}{C_2^{\rm g} + ({\rm T} - {\rm T}_{\rm g})}$$

where T_g is the glass transition temperature of the polymer, and the constants C_1^g and C_2^g have (almost) universal values $C_1^g = 17.4$ and $C_2^g = 51.6$ K. This expression is known as the WLF equation (for Williams Landel and Ferry)

This result is experimentally very useful as it allows us to build up data sets covering very wide effective ranges of timescales on an instrument whose actual range of timescales is much smaller.

Its theoretical significance is that it shows that all the microscopic timescales in the problem of viscoelasticity scale in the same way with temperature; thus we can expect that a microscopic theory of viscoelasticity will contain only a single temperature mobility parameter - a "segment mobility".



Time-temperature superposition for polyisobutylene. On the left is stress relaxation data as a function of time for different temperatures. The data can be collapsed onto a single curve (right) by applying temperature shift factors (inset). The shift factors are given by the WLF relation.

Viscoelasticity: results for monodisperse polymer melts

The relaxation modulus for linear, monodisperse polymer melts of high molecular weight has the following form (shown schematically for two molecular weights)



Log(time)

Note that at short times the curve is independent of molecular weight. For intermediate times there is a wide range of times for which the modulus is essentially constant - this is the *plateau modulus*. The plateau ends at a *terminal time* which does depend on degree of polymerisation, according to a power law $\tau_t \sim N^m$ where the exponent m lies between 3.3 and 3.4.

The storage modulus shows very similar features - here is experimental data for polystyrene:



For times above the terminal time one has essentially viscous behaviour; that is the creep compliance $J(t) \sim t$. We can relate the zero-shear viscosity h0 to the plateau modulus Gp and the terminal time τ_t as $\eta_0 \sim Gp \tau_t$, and as Gp is independent of molecular weight this shows us that the molecular weight dependence of the viscosity should be the same as that of the terminal time, i.e. $\eta_0 \sim N^m$, where we would expect m once again to be between 3.3 and 3.4.

This molecular weight dependence of the viscosity is indeed what is observed above a certain critical molecular weight M_C :



Log(zero shear viscosity) versus Log(molecular weight) for a variety of polymers.

Entanglements

The peculiar viscoelastic properties of polymers are due to the *entanglement* of their chains. We can interpret the plateau modulus as a rubber type elasticity in which instead of having permanent cross-links we have temporary entanglements.

The distance along the chain between entanglements can be estimated from the rubber elasticity formula:

$$G_p = \frac{\rho N_A kT}{M_e}$$

where r is the density of the polymer and M_e is interpreted as the molecular weight between entanglement points.

The entanglements are not permanent, but have a finite lifetime, which is the terminal time.

 M_e is a material constant for a given polymer; it is about twice the value of M_c for the same polymer. A simple-minded interpretation of this is that one needs one entanglement per chain for the viscosity to be dominated by entanglements, and two per chain to see rubber-like elasticity.

The theory of reptation

The physical nature of entanglements was clarified by the *theory of reptation*, due to de Gennes and Doi and Edwards.

The basic constraint felt by one chain due to all the other chains is that it cannot cross the other chains. This effect can be represented by imagining the test chain to be contained inside a *tube*. The motion of the chain is restricted in the lateral direction, but the chain may still wriggle along the tube. This wriggling motion is called *reptation*.



Left: the crosses represent chains coming out of the plane of the paper. The test chain cannot cross these chains, and so it is confined to move in an effective tube (right).

The terminal time is now to be interpreted as the time it takes for the chain to move completely out of its original tube. This can be estimated by noting that within the tube motion is viscous. Thus we can define a segment mobility μ_{seg} . If we were to pull a chain with N segments through the tube the chain mobility would be simply $\mu_{tube} = \mu_{seg}/N$.

Using Einstein's relation we can write down a diffusion coefficient to describe the Brownian motion of the chain inside the tube;

$$D_{tube} = \frac{\mu_{seg}kT}{N}.$$

The chain will completely leave the tube after a time $\tau \sim L^2/D_{tube}$, where L is the length of the tube. But the length of the tube is simply proportional to the length of the chain, which is proportional to N. Thus we predict that $\tau \sim N^3$. The predicted exponent is slightly smaller than the observed value of 3.3.