5.1 Introduction

- So far, we have considered the static configurations and morphologies of polymers, polymer blends and block copolymers
- However, there are a whole class of polymer properties which involve mass transport of polymers, or solvents through polymers (latter covered in lecture 6)
- Various models of polymer dynamics: Rouse, Zimm and Reptation
- Measurements and experimental results
- Computer simulation techniques
5.2 Motivations for studying polymer dynamics

- Polymer deformation and flow behaviour is strongly time dependent: viscoelastic, relaxation time spectrum (cf. Part II course C10)
- Typical morphologies are ‘defect-rich’: non-equilibrium, slow relaxation times
- Need to approach structure formation from a dynamic point of view
- Very important for processing: e.g. extrusion, welding, etc. (cf. Part II course C14)

5.3 Dynamic properties

- What sort of dynamic phenomena are of interest?
  - Viscosity
  - Chain centre-of-mass diffusion in solution
  - Chain centre-of-mass diffusion in the melt
  - Development of weld strength
- Seeking a quantitative microscopic description for observed macroscopic properties
- Before introducing models in detail, we will review some of the experimental data concerning dynamic behaviour of polymers
5.4 Molecular weight dependence of viscosity

Wide range of chemically and structurally dissimilar polymers display the same molecular weight dependence of viscosity.

Abrupt change in the scaling exponent at a certain critical molecular weight.

5.5 Diffusion of polymers in a melt

- In the entangled melt, molecular weight dependence of diffusion coefficient is very strong.
5.6 Diffusion of polymers in dilute solution

- In dilute solution, polymers have a very much weaker dependence of diffusivity on molecular weight.

![Diffusion of polymers in dilute solution diagram]

Behave as hard spheres rather than polymer coils.

5.7.1 The Rouse model

- Applicable to ‘short’ chains in the melt state.
- Consists of a Gaussian worm-like chain which can exchange energy with its surroundings.
- Describe conformation by a contour function $r(s,t)$.
- Subdivide a real polymer into segments, each of which is sufficiently long to obey Gaussian statistics, which have end-to-end distances $a_R$.
- Then, attach these segments together with imaginary springs, representing the entropic restoring forces on the chain as a whole:

$$f = \frac{3k_w T}{\langle \Delta r^2 \rangle} \Delta r$$
5.7.2 The Rouse model

- The equation of motion of the contour function is

\[ m \ddot{r} + \zeta \dot{r} - kr'' = f(s,t), \]

where

\[ \zeta = \text{friction coefficient due to surrounding medium.} \]

\[ k = \frac{3k_B T}{d_R} \text{ due to Gaussian chain entropy.} \]

\[ f(s,t) = \text{Langevin force due to thermal noise:} \]

\[ \langle f(s,t) \rangle = 0, \]

\[ \langle f_i(s_1,t_1) f_j(s_2,t_2) \rangle = 2k_B T \zeta \delta(s_1-s_2) \delta(t_1-t_2) \delta_{ij} \]

5.7.3 The Rouse model

- Sparing the mathematical details, the preceding equation of motion can be solved by neglecting the acceleration term (\textit{i.e.} ignoring chain inertia) and then using Fourier transforms

- The principal results are:
  - Chain centre of mass diffusion coefficient

\[ D_{\text{c.o.m.}} = \frac{k_B T}{\zeta N} \]

  - Longest relaxation time (the \textbf{Rouse time})

\[ \tau_R = \frac{\zeta R_0^4}{3 \pi^2 k_B T a_R^3} \]
5.8.1 The Zimm model

- Applicable to polymers in dilute solution
- Takes into account hydrodynamic drag force on polymer coil due to solvent
- Force acting on polymer coil creates flow field with net component in the same direction as the (primary) force

5.8.2 The Zimm model

- Each particle creates force dragging others along friction coefficient of a spherical colloid (Stokes)
  \[ \zeta = 6\pi R\eta \]
- A group of particles moves more easily than isolated particles under the same total external force
- Consider a polymer coil as such a group of particles or beads
- Whole coil moves as one, including solvent molecules, called a ‘non-draining’ coil (cf. ‘free-draining’)
- Effective hydrodynamic radius of the coil defined by
  \[ R_h = \frac{\zeta_p}{6\pi\eta} \]
5.8.3 The Zimm model

- Friction coefficient of a polymer molecule

\[ \zeta_p = 4\pi \eta R_g \Rightarrow R_h \approx 2 R_g / 3 \]

- Einstein gives \( D = k_B T / 4\pi \eta R_g \Rightarrow D \propto N^{-0.6} \)

- Polymers behave like colloidal particles, same pair distribution function as for a diffusing colloid:

\[ g(r,t) = \left( \frac{1}{4\pi Dt} \right)^{3/2} \exp \left( -\frac{r^2}{4Dt} \right) \]

5.9.1 The reptation model

- Long chain polymer melts contain entanglements between coils, which constrain their movement and therefore their response to mechanical deformation

- The entanglements can be thought of as long bars (for example O₁ and O₂) which pin the chain in 2 dimensions, and from it can only escape by diffusing along its length
5.9.2 The reptation model

- This diffusive wriggling motion, called reptation, governs the time taken by the polymer chains to respond to any applied stress, leading to a non-linear response.
- This can be seen most clearly by measuring the creep compliance of the polymer $J(t)$

\[ J(t) = \frac{e(t)}{\delta \tau} \]

where $t$ is known as the terminal time, $(J_0^e)^{-1}$ is known as the plateau modulus.

5.9.3 The reptation model

- This non-linear behaviour can be explained to an extent by a simple scaling argument based on the time taken for a chain to escape a fictitious sock-like tube representing the confining effects of the entanglements.
- This escape time is identified with the terminal time.
5.9.4 The reptation model

- If the each segment of the chain has mobility $\mu_1$, then the mobility of the chain moving longitudinally in the tube is given by:

$$\mu_{\text{tube}} = \frac{\mu_1}{N}$$

- Therefore the tube diffusion coefficient can be calculated from a Roussian relationship as:

$$D_{\text{tube}} = \frac{\mu_1 T}{N} = \frac{D_1}{N}$$

- And so the time taken for the chain to diffuse over a length comparable to the length of the tube is:

$$T_t \approx \frac{L^2}{D_{\text{tube}}} = \frac{NL^2}{D_1} \propto N^3$$

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5.9.5 The reptation model

- During this terminal time, the chain c.o.m. moves by a distance $L$ in a tube of diameter $d$, hence:

$$\langle \Delta r^2_{\text{c.o.m.}} \rangle \approx Ld$$

$$\therefore D = \langle \Delta r^2_{\text{c.o.m.}} \rangle / T_t = \frac{LdD_1}{NL^2} \propto N^{-2}$$

- This is a much stronger dependence than the Roussian relationship ($D \sim N^{-1}$) for shorter, unentangled chains.

- The cross-over in diffusion behaviour as a function of molecular weight can now be understood.
5.9.6 The reptation model

- The prediction that the terminal time (and therefore the shear viscosity) scales with $N^3$ is in reasonable agreement with experiment ($N^{3.3}$).
- Also, assuming a value for the segmental mobility of order $10^{-11}$ seconds leads to a terminal time of order 10 seconds for a chain with $10^4$ segments.
- This is entirely plausible for real polymers, and implies that any process which acts over similar timescale to terminal time will need to take into account orientation effects induced by the flow field.

5.10 Molecular weight dependence of viscosity

Wide range of chemically and structurally dissimilar polymers display the same molecular weight dependence of viscosity.

Abrupt change in the scaling exponent at a certain critical molecular weight.
5.11 Direct observation of reptation

- Manipulation of DNA with ‘optical tweezers’
- After a brisk tug, the stained chain relaxes back along the path of its reptation tube

Reptation tubes really exist!
Not just a convenient theoretical construct

5.12 Indirect measurement of polymer dynamics

- **Dynamic structure factor** $S(q,t)$ probes the time correlation of scattering amplitudes

$$S(q,t) = \langle C(q,t'+t)C(q,t) \rangle / N$$

- Measure $S(q,\omega) = \text{F.T.}\{ S(q,t) \}$
  - Neutron scattering $E = 10^{-2} \text{ eV}$ $\Delta E = 10^{-6} \text{ eV}$
  - Light scattering $E = 1 \text{ eV}$ $\Delta E = 10^{-8} \text{ eV}$
  - Synchrotron X-rays $E = 10^{4} \text{ eV}$ $\Delta E = 10^{-1} \text{ eV}$

- Dynamic light scattering: photon correlation techniques
- Dynamic neutron scattering: spin-echo measurements
- Direct observation by fluorescent staining
5.13.1 Neutron spin echo technique

- A direct way to measure dynamic structure factor

\[ S(q, t) = \int \exp(i\omega t)S(q, \omega)d\omega \]

- Neutron beam with range of energies
- Pass through a magnetic field \( H \Rightarrow \) spins precess by amount proportional to their energy
- Quasielastically scattered by sample
- Pass through field equal and opposite to \( H \Rightarrow \) spins precess backwards to a degree which is retarded by energy loss to sample
- Record integrated scattering at particular \( q \) value

5.13.2 Neutron spin echo measurements

- Quasielastic neutron scattering on melt of poly(ethylene-co-propylene) at 199°C, \( M_w = 86,000 \)
- Shows deviation from Roussian behaviour at long relaxation times

![Graph](image)
5.14 Dynamic light scattering

- DLS scattering from solution of PS in dioxane
- Shows $S(q,t)$ as a function of $t$ at different $q$. Short wavelength modes relax faster

5.15 Computer simulation of polymer welding

- Recall from lecture 3 that polymer interfaces tend to be quite weak as entropy of mixing is low
- We can use computer simulations to quantify the strength of polymer welds by looking at chain interdiffusion
5.16.1 Characterising weld strength

- Calculate number of segments crossing weld-line $N_w$

$$N_w \sim t^{1/4}$$
$$N_{w_{eqm}} \sim N^{1/2}$$
$$t_w \sim N^3$$

$$\Rightarrow N_w \sim N^{-1/4}t^{1/4}$$

$cf. K_{lc} \sim N^{-1/4}t^{1/4}$

5.16.2 Characterising weld strength

- Comparison of the form of $N_w$ with critical stress intensity factor $K_{lc}$ calculated experimentally indicates the two have same functional dependence on $N$ and $t$

- This means that $N_w$ is an effective microscopic measure of weld strength

- We have not taken into account the effect of interface area on the weld strength

- We have also assumed that weld is formed between chemically similar polymers in an ideal melt state
This lecture we discussed three different models for the dynamics of a polymer coil: Rouse, Zimm and reptation models.

Roussian chains are short, unentangled and have a moderate dependence of diffusivity on molecular weight.

In dilute solution, the Zimm model predicts a diffusivity which is related to the effective hydrodynamic radius of the polymer coil, and is only weakly dependent on molecular weight.

The reptation model deals with entangled chains in the melt state, and has a very strong dependence on molecular weight.