Recall: Polymers are essentially entropic springs

Polymers perform a random walk with effective step size b>a=monomer length.

The mean end-to-end distance is:

$$\langle \mathbf{r}^2 \rangle = Nb^2$$

 $\langle \mathbf{r}^2 \rangle$ is Gaussian distributed resulting in an entropy:

$$S(\overline{R}) = -\frac{3k_BR^2}{2Na^2} + const \implies F(\overline{R}) \propto \frac{3k_BTR^2}{2Na^2}$$

Thus the polymer acts as an entropic spring with spring constant

$$k_{spring} = \frac{3k_BT}{Na^2}$$

Obs. error in Polymers I slides

Recall: Excluded volume in solutions





R

Assume polymer of N segments occupy a volume R^3 Uniformly distributed and with no correlations. Each segment excludes a volume v Probability of another monomer being within v is vN/R³ Energy cost (due to entropy reduction) is k_BT per exclusion.

For all N segments this energy contribution (assuming $v \approx a^3$) is; $F_{rep} = k_B a^3 T N^2 / R^3$ (expansion).

From before: entropic force; $F_{el} = k_b T3R^2/2Na$

$$\frac{\partial}{\partial R} \left(F_{rep} + F_{el} \right) = 0 \implies R \propto a N^{3/5} \quad \text{``A swollen coil''}$$

However, in a polymer melt the concentration of segments is uniform due to space filling. No swelling!

Recall: reptation in polymer melt



Picture the polymer as confined into a tube by the entanglements of its neighbours. The chain performs a 1D random walk. Each segment has a mobility, μ_{seg} , according to the drag force of its environment. The total mobility is thus $\mu_{chain} = \mu_{seg}/N$ The 1D diffusion coefficient is given by the Einstein relation

$$D_{tube} = k_B T \mu_{chain} = k_B T \mu_{seg} / N$$

The time it takes for polymer to escape its tube is given by

$$\tau_T = L^2 / D_{tube} \propto N^3$$
 $\overset{\text{Clower}}{=}$

Close to the exp. results!

Modifications: Constraint release and contour length fluctuations



treat entanglements as temporary cross-links

$$G = \frac{\rho RT}{M_e}$$

Recall: rubber plateau

At the rubber plateau the liquid behaves as a rubber. The magnitude of the plateau is independent of N. For t<< τ_T the entanglements acts as cross-links. Use theory of rubber elasticity. •Affine deformation •1D elongation •incompressibility $\tau = nk_BT \left[(1+e) - \frac{1}{(1+e)^2} \right]$ expand for small e $E = 3nk_BT \Rightarrow G = nk_BT = \frac{\rho RT}{M_x}$

where ρ is the density, *R* the gas constant and *M*_e is the relative molecular weight between entanglements.

Today: More about polymer solutions and polymeric crystals

•As we have seen pure polymers represents the simple, "the ideal" case.

•However, more often we encounter polymers in solutions. From dilute to concentrated solutions with complicated behaviour on temperature and the properties of the solvent and the solute.

•The polymers in solutions can be very long, overlapping, entangled and sometimes even cross linked with physical or chemical cross links.

Polymer solutions

Polymers in solutions are a major topic in polymer science – applied as well as theoretical.

- Polymer segments in a solution have an interaction energy with other (near by) segments apart from covalent bonding: w_{pp}
- In a similar way we have an interaction energy between the solvent molecules: w_{ss}
- When the polymer becomes disolved we have a new interaction energy between solvent and polymer: w_{ps}

A χ -parameter for polymer solutions

Following the arguments from chapter 3 we derive an expression for the mixing when new p-s contacts are made and old p-p and s-s contacts are lost:

$$\chi = \frac{z}{2k_B T} \left(2w_{ps} - w_{pp} - w_{ss} \right)$$

The internal energy U will change with the addition of polymer to a solvent:

$$\Delta U_{\rm int} = -k_B T 2 \nu \chi \frac{N^2}{R^3} + \text{const}$$



The good the bad and the theta

Combining the new expression for ΔU_{int} with the previous for coil swelling and entropic elastic spring:

$$F_{el} + F_{rep} + \Delta U_{int} = \frac{3}{2} k_B T \frac{R^2}{Na} + k_B T v (1 - 2\chi) \frac{N^2}{R^3}$$

The value of x determines if excluded volume effects are dominating or counteracted by the p-s interaction: When x<1/2 the coil is swollen (A good solvent) When x>1/2 the coil forms a globule (A bad or poor solvent) When x=1/2 the two energies cancel and we have a "theta solvent" with pure random walk conformation!

Experimental proof



Scattering Intensity, I \propto q^{-1/\nu} or I^{-1} \propto q^{1/\nu}

The coil-globule transition



The size of DNA coil and even globule can be of order of the wavelength of visible light (400-700 nm, N up to $\sim 10^{10}$). Conformational changes in DNA can be seen by *optical microscope*.

With large N the size difference between the swollen coil with $R \sim N^{0.6}$ and the globule with $R \sim N^{1/3}$ is enormous.

Applications possible in many different fields: For example a "nano-motor"

The transition from an expanded coil to a globule can be initiated by changing χ .

$$\chi > 1/2$$

Changes in temperature or pH can be used to make the polymer coil expand and contract.

Three concentration regimes in polymer solutions (good solvents)

In the dilute regime there is a minimum of interaction between the coils







Con. solution $c > c^*$

Dilute solution $c << c^*$ /

Semi-dilute solution $c=c^*$

In the semi-dilute regime coils starts to overlap at a concentration $c^* \sim N/R^3$.

In a good solvent thus $c^* \sim N^{-4/5}$ ($\chi < 1/2$).

Above c~c* space filling begins to decrease the excluded volume effect despite the goodness of the solvent. (Scaling theory)

The scaling method

Scaling arguments are frequently used in polymer science. What can we expect about the shrinking of coils above c* in good solvents?

1. Assume that $R = aN^{3/5}f(c/c^*)$ for $0 < c/c^* < 1$

2.
$$f(c/c^*) \approx 1$$
 for $c/c^* << 1$

2.
$$f(c/c^*) \approx const \cdot (c/c^*)^n$$
 for $c/c^* >> 1$

Thus at c>>c*: R=const•aN^{3/5} (c/c*)ⁿ = const aN^{3/5}(c/N^{4/5})ⁿ

(since $c^* \approx N^{-4/5}$ in a good solvent)

From R=aN^{1/2} at c = 1 we get 3/5+(4/5)n=1/2, n=-1/8 and for c>c*:

R~aN^{3/5}(c/c*)^{-1/8}~aN^{3/5}(cN^{4/5})^{-1/8}~aN^{1/2}c^{-1/8}

Entangled polymer solutions

- Polymer melts and polymer solutions above c* can entangle resulting in:
- High viscosity (reptation a related subject)
- Memory effects
- Viscoelasticity (elastic at high frequency, viscous at low frequencies).
- From last week: Not all contacts between overlapping chains are entanglements. Empirically N_e is found to be in the interval 50-500 reflecting that not every contact are entangled: $G = \frac{\rho RT}{G}$

An entangled polymer melt or solution can be seen as a transient polymer network

Crystallinity: Polymer molecules show some degree of ordering. Depending on molecular symmetry (tacticity), molecular weight (kinetics) and branching, etc.



Glassy: molecules in a random coil conformation. For example fully amorphous PMMA and PPO

$10~\mu m$ x $10~\mu m$



Microscopy image of a crystal of high density poly(ethylene) - viewed while "looking down" at the lamella.

Lamella grows outwards





Polymers with some symmetry are usually polycrystalline. They are usually never completely crystalline but have some amorphous regions and "packing defects".

Several crystals of isotactic poly propylene G. Ellis*, M. A. Gómez and C. Marco

Why is the lamellar crystal a basic unit?

competition between polymer chain stretching and coiling on one hand and on reduction in free energy for crystal formation on the other hand determines lamellar thickness.

 τ^{-1} is a microscopic frequency, Δg is negative by definition

Calculating the maximum net rate for a crystal of thickness I gives an estimate of the optimal thickness (fastest growing).

Lamellar thickness of PE grown from a melt

Lamellar Thickness:

$$L_c = \frac{2\sigma T_m^0}{\Delta H_v (T_m^0 - T_c)}$$

- σ Surface energy
- T_m^0 Equilibrium melting Temperature
- ΔH_{v} Enthalpy of fusion per unit volume
 - T_c Crystallization temperature

Micellar Structures

When diblock copolymes are asymmetric, lamellar structures are not favoured.

Instead the shorter block segregates into small spherical phases known as "micelles".

Interfacial "**energy cost**": $\gamma(4\pi r^2)$

Reduced stretching energy for shorter block

Density within phases is maintained close to bulk value.

Mixing polymers Generally polymers don't mix - why?

(two molecular liquids)

Free energy of mixing: $\frac{F}{k_B T} = \phi_A \ln \phi_A + \phi_B \ln \phi_B + \chi \phi_A \phi_B$ interaction energy entropic

regular solution model

Interaction parameter χ : χ < 2 always single phase χ > 2 phase separation

Mixing polymers Generally polymers don't mix - why?

For two polymer with N monomers

$$\frac{F^{pol}}{k_B T} = \phi_A \ln \phi_A + \phi_B \ln \phi_B + N \chi \phi_A \phi_B$$

$$\frac{F^{mon}}{k_B T} = \frac{\phi_A}{N} \ln \phi_A + \frac{\phi_B}{N} \ln \phi_B + \chi \phi_A \phi_B$$

(Flory-Huggins free energy)

Interaction parameter χ : $\chi < 2/N$ always single phase $\chi > 2/N$ phase separation

N is usually $\approx 10^3 - 10^6$ -> even for small χ we get macro-phase separation

Block copolymers

Blocks of different polymers covalently linked together

Even if $\chi < 2/N$ the system cannot macro-phase separate (similar to amphiphiles)

Block copolymers

Asymmetric structures -> more complex morphology

Fig. 9.11 A lamellar morphology (top) is less favoured for an asymmetric diblock copolymer, as it requires the two blocks to be stretched to different degrees. Instead, a morphology with curved interfaces (bottom) is favoured.

Exotic Morphologies

Fig. 9.12 Some block copolymer morphologies. The most commonly observed phases are shown as L, C, and S—lamellae, cylinders, and spheres respectively. PL, G, and D (perforated lamellae, gyroid, and double diamond respectively) are more complex phases that have been more recently identified. Diagram courtesy of M. Matsen.