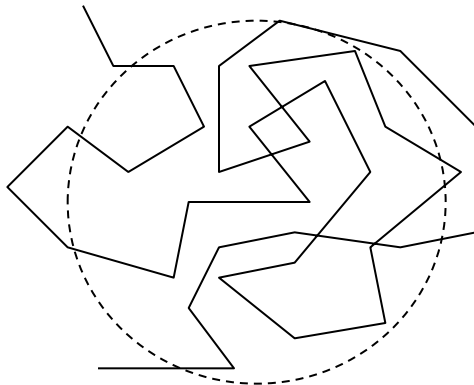


Polymers in Solution

- A polymer is a molecule comprised of many similar units. Unlike simple molecules polymers do not have a unique molecular weight but have a distribution. When dissolved in solution the molecules swell up to much larger dimensions.



- There are two ways by which we can define the dimensions of a polymer chain, one is the root mean square end to end distance, $\langle r^2 \rangle^{1/2}$, or the root mean square distance of the elements of the chain from its centre of gravity, $\langle s^2 \rangle^{1/2}$, also known as the radius of gyration. These two parameters can be linked by the simple expression

$$\langle r^2 \rangle^{1/2} = \langle 6s^2 \rangle^{1/2} \text{ --- 3.1}$$

Polymers in Solution

- A simple model of a polymer chain consists of a series of x links of length, l , joined in a linear sequence, with no restrictions on the bond angle. Using this model the end to end distance is proportional to the square root of the number of links:

$$\langle r^2 \rangle^{1/2} = lx^{1/2} \text{ --- } 3.2$$

- Thus the size of a polymer molecule is proportional to the square root of its molecular weight.

- The radius of gyration is more often quoted experimentally because it can be measured experimentally, using light scattering, sedimentation, etc.
- Radius of gyration for PEO

Molecular weight	$\langle r^2 \rangle^{1/2}$ nm	$\langle s^2 \rangle^{1/2}$ nm
100,000	12.1	4.9
200,000	16.7	6.8
1,000,000	38.0	15.5
5,000,000	85.6	35.0

Polymer Molecular Weight

- Polymers do not have a unique molecular weight, they have a distribution. The average of that distribution depends on how you calculate (measure) the molecular weight.
- Number average Molecular weight (osmotic pressure)

$$M_N = \frac{\sum_i n_i M_i}{\sum_i n_i}$$

Weight Average Molecular weight (light scattering)

$$M_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i M_i}{\sum n_i M_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

n_i and w_i are the number and weight fractions respectively

M_w is always $> M_N$ and the ratio M_w/M_N is often taken as a measure of the molecular weight distribution

What do the Weights Mean?

M_n : This gives you the number average molecular weight

Let's say you had the following polymer sample:

2 chains:	1,000,000	2,000,000
5 chains:	700,000	3,500,000
10 chains:	400,000	4,000,000
4 chains:	100,000	400,000
2 chains:	50,000	<u>100,000</u>
		10,000,000

$$M_n = 435,000$$

$$10,000,000/23 = 435,000$$

Weight Average Molecular Weight

M_w : Since most of the polymer mass is in the heavier fractions, this gives the average molecular weight of the most abundant polymer fraction by mass.

$$\frac{2,000,000}{10,000,000} = 0.20 \times 1,000,000 = 200,000$$

$$\frac{3,500,000}{10,000,000} = 0.35 \times 700,000 = 245,000$$

$$\frac{4,000,000}{10,000,000} = 0.40 \times 400,000 = 160,000$$

$$\frac{400,000}{10,000,000} = 0.04 \times 100,000 = 4,000$$

$$\frac{100,000}{10,000,000} = 0.01 \times 50,000 = 500$$

$$\mathbf{M_w} = 609,500$$

Polymers in Solution

- **Thermodynamics of Simple Liquid Mixtures**

- From the condition for equilibrium between 2 phases may be derived the free energy for dilution of a solution,

$$\Delta G_A = kT \ln \left(\frac{p_A}{p_A^0} \right) \text{---3.3}$$

- Where ΔG is the free energy of dilution, resulting from the transfer of one molecule of liquid A from the pure liquid state with vapour pressure p_A^0 to a large amount of solution with vapour pressure, p_A .

- **Ideal Solutions**

- Assuming the molecules of component A and B have roughly the same size, shape and interactions. They may then form an ideal solution, defined as one in which Raoult's Law is obeyed, which states that the partial pressure of each component is equal to its mole fraction, n , thus

$$\Delta G_A = kT \ln n_A \text{---3.4}$$

Polymers in Solution

- So that the total free energy of mixing is

$$\Delta G = N_A \Delta G_A + N_B \Delta G_B$$

$$\Delta G = kT(N_A \ln n_A + N_B \ln n_B) \text{ --- 3.5}$$

N is the number of molecules

- The conditions for ideal mixing $\Delta H=0$ so that the entropy of mixing is given by

$$\Delta S = -k(N_A \ln n_A + N_B \ln n_B) \text{ --- 3.6}$$

- Which is positive for all compositions, so that by the

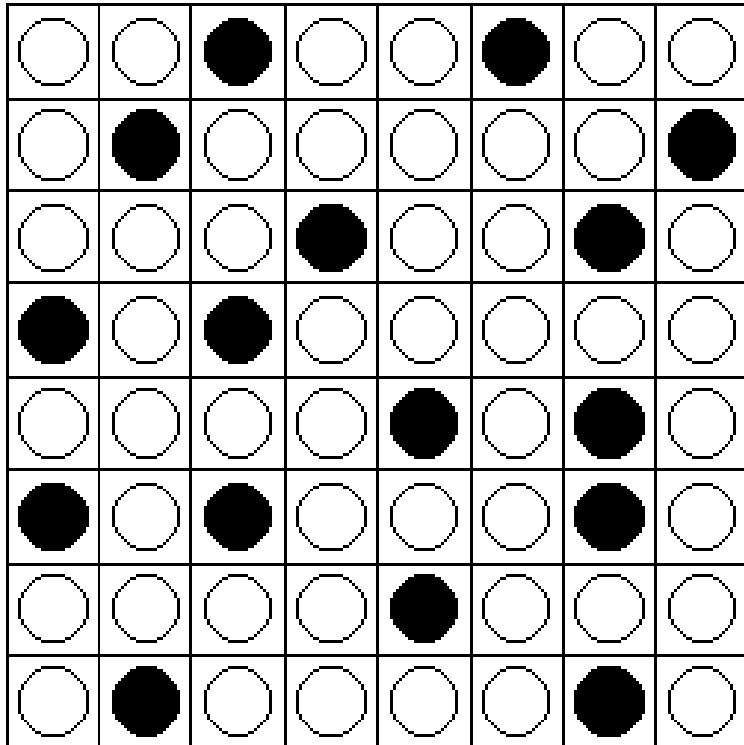
2nd law spontaneous mixing occurs in all proportions

- **Other types of Mixing**

In practice few systems obey Raoult's Law and deviations may occur.

1. **Athermal Solutions** where $\Delta H=0$ but ΔS no longer given by Eqn 3.6
2. **Regular Solutions** where ΔS has the ideal value, but ΔH is finite
3. **Irregular Solutions** where both ΔH and ΔS are non ideal.

A mixture of two liquids



Let us construct a lattice with 64 lattice sites and put 48 molecules of solvent A and 16 molecules of solvent B.

The entropy is now given by

$$\Delta S = k(N_A \ln n_A + N_B \ln n_B) \dots 3.6$$

where $N_A = 48$, $N_B = 16$, $n_A = 0.75$, $n_B = 0.25$,

Polymers in Solution

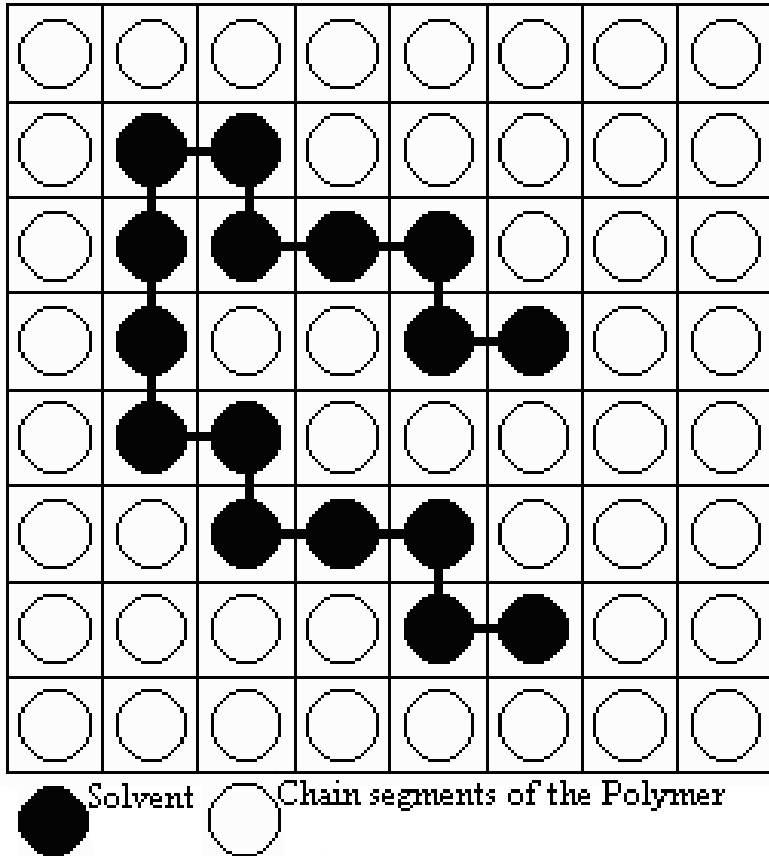
Now let us construct a lattice with 64 lattice sites and put 48 molecules of solvent A and 1 molecule of polymer B.

The entropy is now given by

$$\Delta S = k(N_A \ln \phi_A + N_B \ln \phi_B) \dots 3.6$$

where $N_A=48$, $N_B=1$, and ϕ_A the volume fraction of solvent =0.75, ϕ_B , the volume fraction of polymer=0.25.

Thus the entropy of the polymer is considerably less compared to the solution



Polymers in Solution

- Ideal solutions assume that all intermolecular interactions in a solution are the same, so that the enthalpy of mixing is zero. The simplest correction is to introduce a parameter ($\Delta\epsilon$) that is a measure of the difference between like-unlike and like-like molecular interactions, where

$$\Delta\epsilon = \epsilon_{A,B} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB}) \quad \text{--- 3.7}$$

- This gives the Enthalpy of mixing of mixtures A and B as

$$\Delta H_{mix} = zN_A n_B \Delta\epsilon \quad \text{--- 3.8}$$

Defining

$$\chi = \frac{z\Delta\epsilon}{kT} \quad \text{--- 3.9}$$

- We obtain

$$\Delta H_{mix} = kTN_A n_B \chi \quad \text{--- 3.10}$$

Polymers in Solution

- For polymer solutions we use the same arguments but replace the mole fraction of component B, by the volume fraction of polymer present, ϕ_B .
- i.e

$$\Delta H_{mix} = kTN_A\phi_B\chi \text{ --- 3.11}$$

- So that the total free energy of mixing is given by

$$\Delta G = kT(N_A \ln \phi_A + N_B \ln \phi_B + \chi N_A \phi_B) \text{ --- 3.12}$$

- From equation 3.11 it can be seen that as long as χ is positive, which it virtually always is, the enthalpy of mixing is always positive, and is unfavourable. Thus one would expect phase separation to occur on cooling, since on cooling the entropic term is reduced. This is indeed what one observes in many systems. However, as we know from cooking eggs *etc.*, this is not true. In fact for water soluble polymers this is not true at all.

Polymers in Solution

- The reason being that in our analysis we have assumed that χ is independent of temperature. This is not true for water as a solvent due to H-bonding, which decreases as the temperature increases.
- From equation 3.12 we can estimate the change in chemical potential on mixing a polymer

$$\mu_A - \mu^0 = \left(\frac{d\Delta G}{dN_1} \right)_{N_B}$$

$$= kT \left[\ln \phi_A + \left(1 - \frac{1}{x} \right) \phi_B + \chi \phi_B^2 \right] \dots 3.13$$

- Where x is the number of segments of polymer. If the logarithmic term in eqn. 3.13 is expanded and only low powers of the polymer volume fraction ϕ_B are retained we end up with a virial expansion

Polymers in Solution

$$\mu_A - \mu^0 = kT \left[\frac{\phi_B}{x} + \left(\frac{1}{2} - \chi \right) \phi_B^2 + \dots \right] \quad \text{---3.14}$$

- Or in terms of osmotic pressure, Π

$$\Pi = \frac{kT}{V_A} \left[\frac{\phi_B}{x} + \left(\frac{1}{2} - \chi \right) \phi_B^2 + \dots \right] \quad \text{---3.15}$$

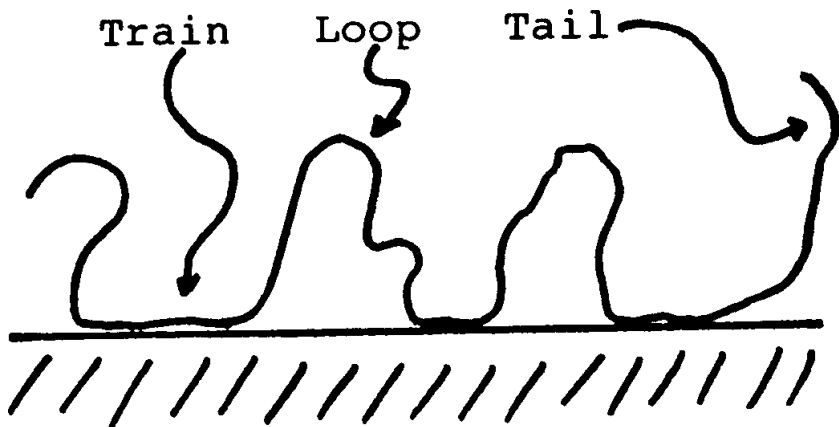
- This is very analogous to the virial equation for gases. The 1st term is the ideal term and the 2nd a non-ideal term. It can be seen that when $\chi = 0.5$ the properties of polymer solution are ideal. This is known as the θ condition.

- It turns out that when $\chi < 0.5$, the polymer dissolves the solvent is known as a good solvent, but when $\chi > 0.5$, the polymer does not dissolve and the solvent is a poor solvent.

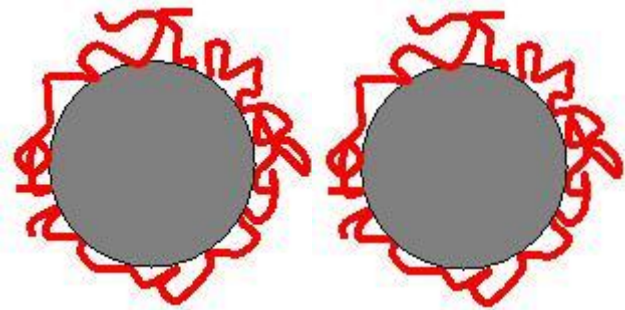
Polymer adsorption

- When polymers adsorb to a surface they generally do not lay flat on the surface, but extend away from the surface as well. The polymer segments thus exist as a series of tails, loops and trains as shown

below.



- This means that when polymers are adsorbed onto particle surfaces, they may interfere with each other before van der Waals forces play a significant role and aggregate the particles



Polymer adsorption

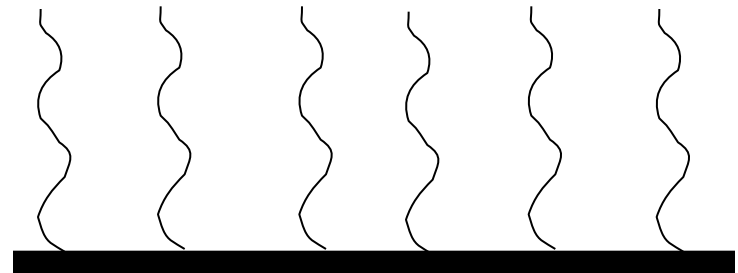
- In the above case the adsorbed polymer provides a physical buffer, which prevents the cores of the particles from coming together and hence prevents the van der Waals forces being significant. A polymer when it is adsorbed to a surface generally does not form a compact layer, but a fuzzy, relatively thick monolayer is formed, a bit like a ball of cotton wool. The polymer layer itself may only contain around 5% polymer, the rest is solvent.
- The criteria for polymer to be a good stabilising agent is for it to be strongly adsorbed onto the surface and to extend sufficiently far away from the surface (5-10nm) for van der Waals forces to be less than kT . These conditions are mutually exclusive for homopolymers, i.e. a polymer that is made of only one component. If the polymer adsorbs too strongly it will lay flat on the surface and the van der Waals forces will be significant, whilst the other limiting condition is such that the polymer will not adsorb at all

Polymer adsorption

- If the polymer is comprised of two parts, where on part of the polymer will adsorb onto the surface and the other not, then a good stabiliser will be prepared. Such materials are called copolymers and block and graft copolymers are materials that fulfil this role well. They are in effect similar to surfactants.



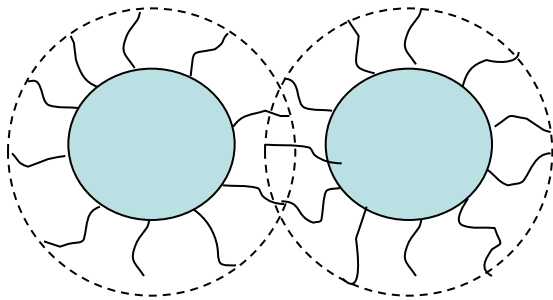
An AB Block Co-polymer



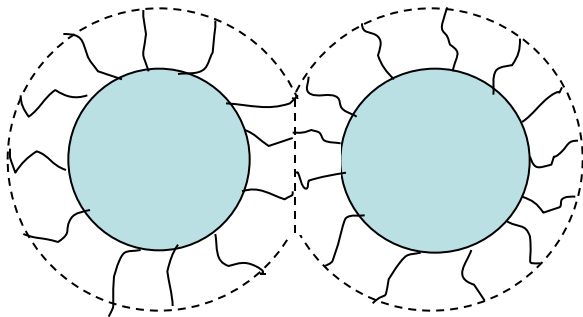
A Graft or Comb copolymer

Interactions between adsorbed Polymer layers

- When two particles coated with polymers interact the two polymer layers overlap and compress. This has two effects one osmotic, enthalpic, and one entropic. The osmotic effect is that the concentration of polymer in the gap is increased, this increases the osmotic pressure and the particles are forced apart. The entropic effect is a consequence of the compression of the polymer layer decreasing the number of configurations the polymer can adopt. Both effects have been quantified but the theory is not as good as that of double layers or van der Waals interactions



Overlap of adsorbed layer



Compression of adsorbed layer

Interactions between adsorbed Polymer layers

- In the simplest approach, it is assumed that the total interaction is simply the sum of the osmotic and entropic components.

$$\Delta G_{mix} = \frac{2\pi RkTV_p^2 n^2 \Gamma^2 (\frac{1}{2} - \chi)}{V_l} S_{os} - -3.16$$

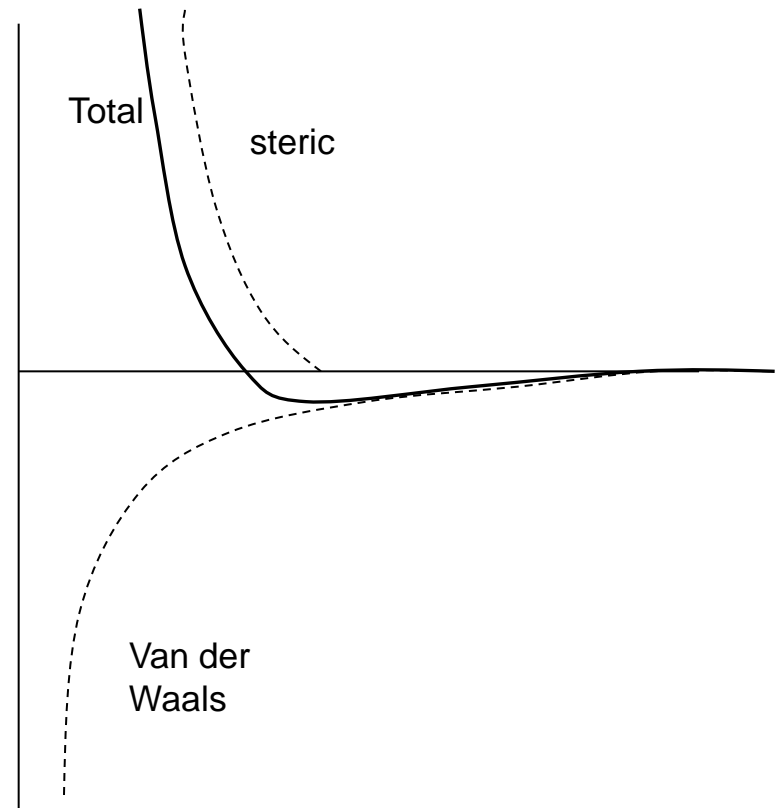
- Where V_p and V_l are the molar volume of the polymer segments and the liquid respectively, n is the number of polymer segments overlapping and Γ is the amount of polymer adsorbed, and S_{mix} is a geometric term that depends on the particle size and the thickness of the polymer layer.

- Inspection of eqn. 3.16 shows that the sign of the free energy of mixing depends on the value of χ , the Flory-Huggins interaction parameter. If $\chi > 0.5$ then the mixing term is -ve and an attraction is seen, if $\chi < 0.5$, then the mixing term is positive and we get a repulsive interaction, and if $\chi = 0.5$ then the mixing term is zero.
- The entropic term is always repulsive though since as the surfaces come closer together the number of configurations the polymer can adopt is reduced.

Interactions between adsorbed Polymer layers

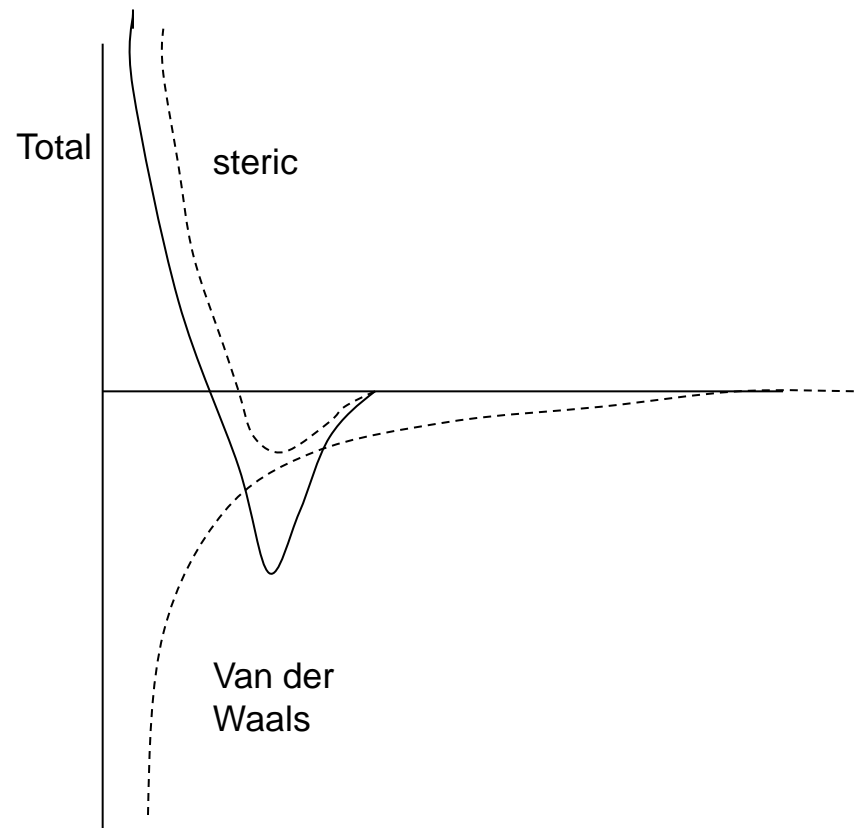
$$\Delta G_{ent} = 2\pi RkT\Gamma.S_{ent} \text{ --- 3.17}$$

- Where S_{ent} is another geometric term.
- Opposite is the total interaction curve, including van der Waals forces when the χ parameter < 0.5 . Note that the depth of the minimum may be adjusted by changing the thickness of the polymer layer (Molecular weight).



Interactions between adsorbed Polymer layers

- Opposite is the total interaction curve, including van der Waals forces when the χ parameter > 0.5



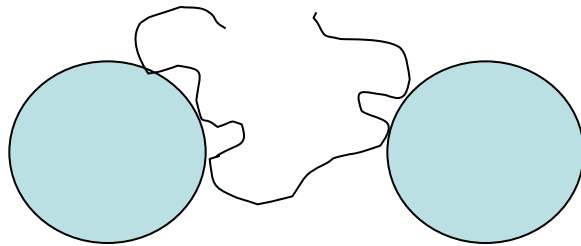
Interactions between adsorbed Polymer layers

- We can see from these graphs that the type of interaction attraction or repulsion, is dependent on the value of the χ parameter. The χ parameter itself is dependent on temperature as we have seen, thus flocculation (aggregation) of particles is also dependant on temperature. Since χ decreases as T increases for most solvent soluble polymers the same is true regarding flocculation.
- For water soluble polymers the opposite is true

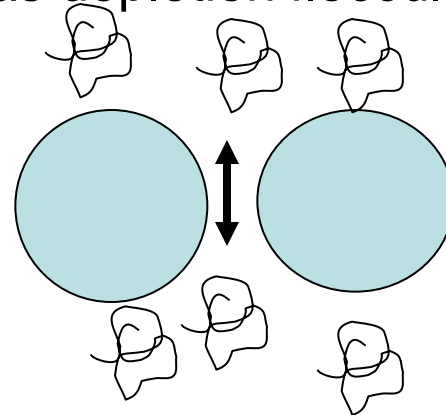
Stabilising Polymer	M.Wt	Dispersion Medium	Flocculation Temperature	Θ Temperature
Polyethyleneoxide	1 400	0.39M MgSO ₄	317 K	330 K
Polyethyleneoxide	4 700	0.39M MgSO ₄	320 K	327
Polyethyleneoxide	10 000	0.39M MgSO ₄	318 K	319
Polyethyleneoxide	13 500	0.39M MgSO ₄	318 K	315
Polyethyleneoxide	23 000	0.39M MgSO ₄	314 K	315
Polyacrylic acid	9 800	0.2 M HCl	287 K	287
Polyacrylic acid	19 300	0.2 M HCl	289	289
Polyacrylic acid	51 900	0.2 M HCl	283	287
Polyacrylic acid	89 700	0.2 M HCl	281	287
Polyvinylalcohol	26 000	2.0M NaCl	320 K	300
Polyvinylalcohol	57 000	2.0M NaCl	301	300
Polyvinylalcohol	270 000	2.0M NaCl	312	302
Polyacrylamide	18 000	2.1M (NH ₄) ₂ SO ₄	292 K	290
Polyacrylamide	60 000	2.1M (NH ₄) ₂ SO ₄	295	290
Polyacrylamide	180 000	2.1M (NH ₄) ₂ SO ₄	280	290

Flocculation of Particles by Polymer

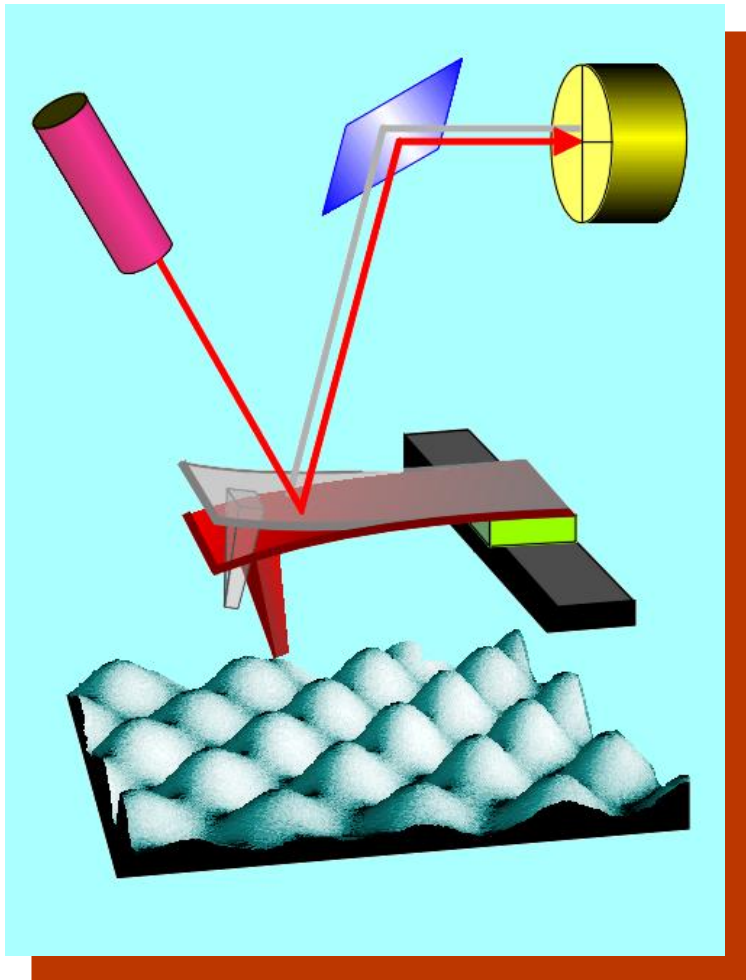
- Under some circumstances polymers can flocculate particles. Under very dilute polymer concentrations of polymer, so that the particles are not fully covered by polymer, aggregation occurs by one polymer molecule bridging between two particles



Also if the polymer is non adsorbing, when the gap between two particles becomes less than the dimension of the polymer, there will be less polymer between the two particle surfaces than in the bulk. Thus solvent will flow from the dilute to the concentrated region. This is brought about by the particles moving towards each other. This is known as depletion flocculation.

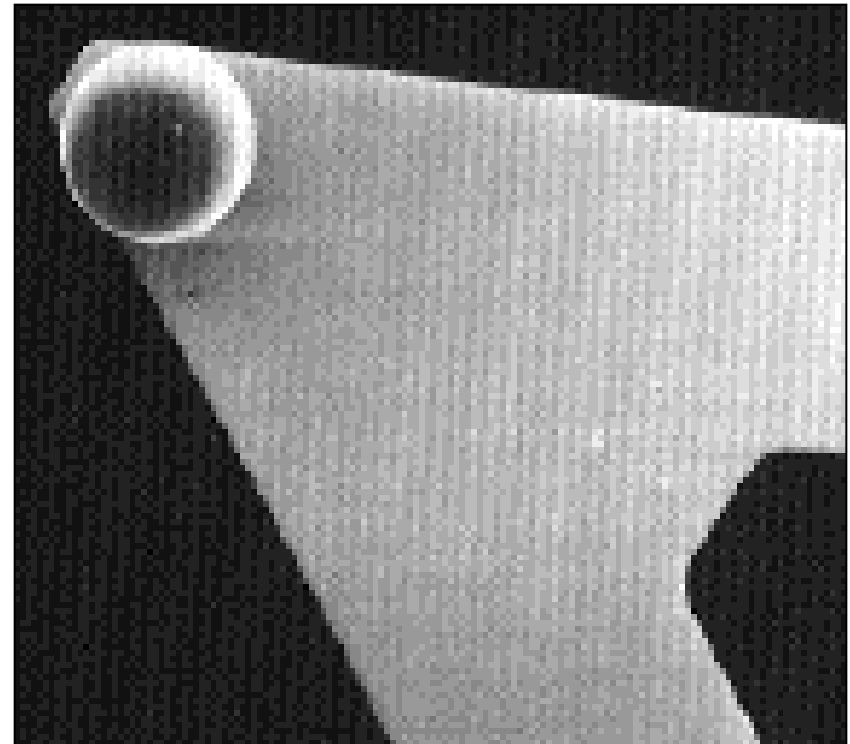
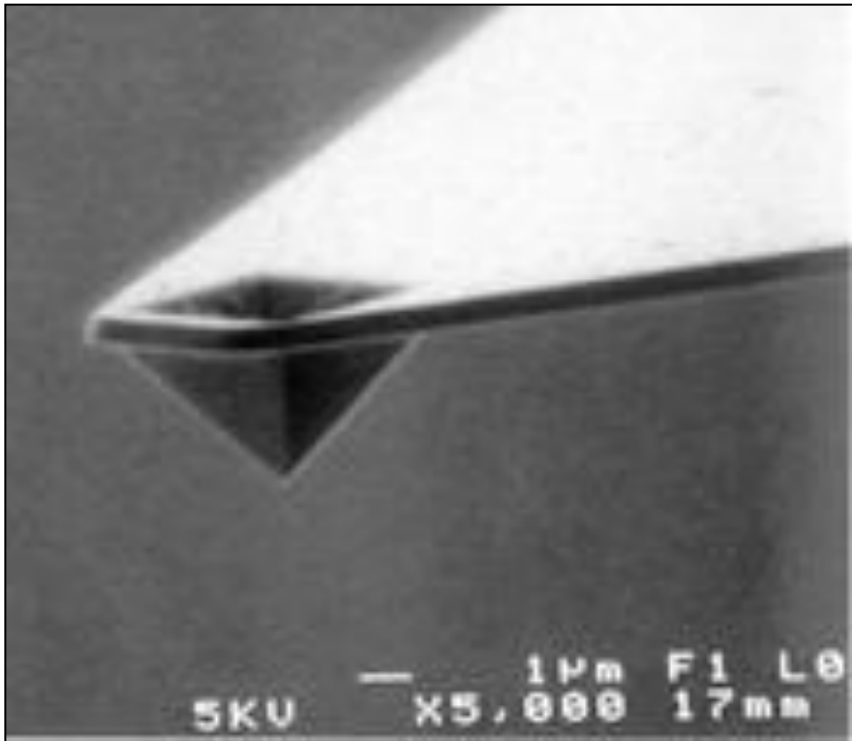


Measurement of particle interactions



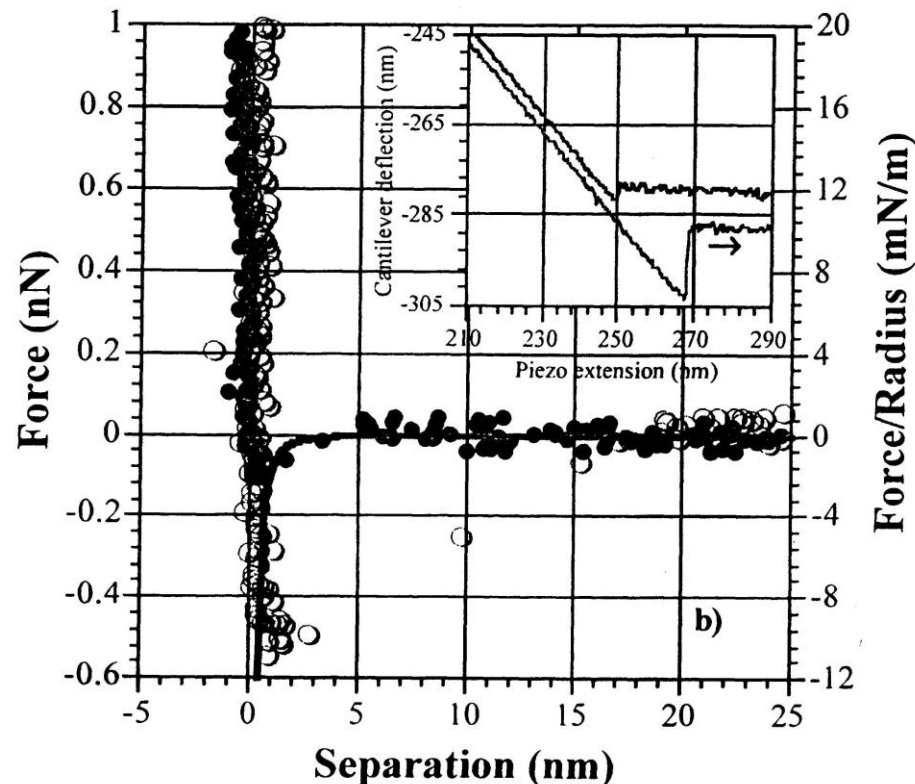
- Particle interactions can be measured by modifying an atomic force microscope. In this experiment the interaction between a sharp tip attached to the end of a cantilever can be determined by monitoring the bending of the cantilever using laser light. By replacing the tip by a particle, particle surface and particle-particle interactions can be measured.

Measurement of particle interactions

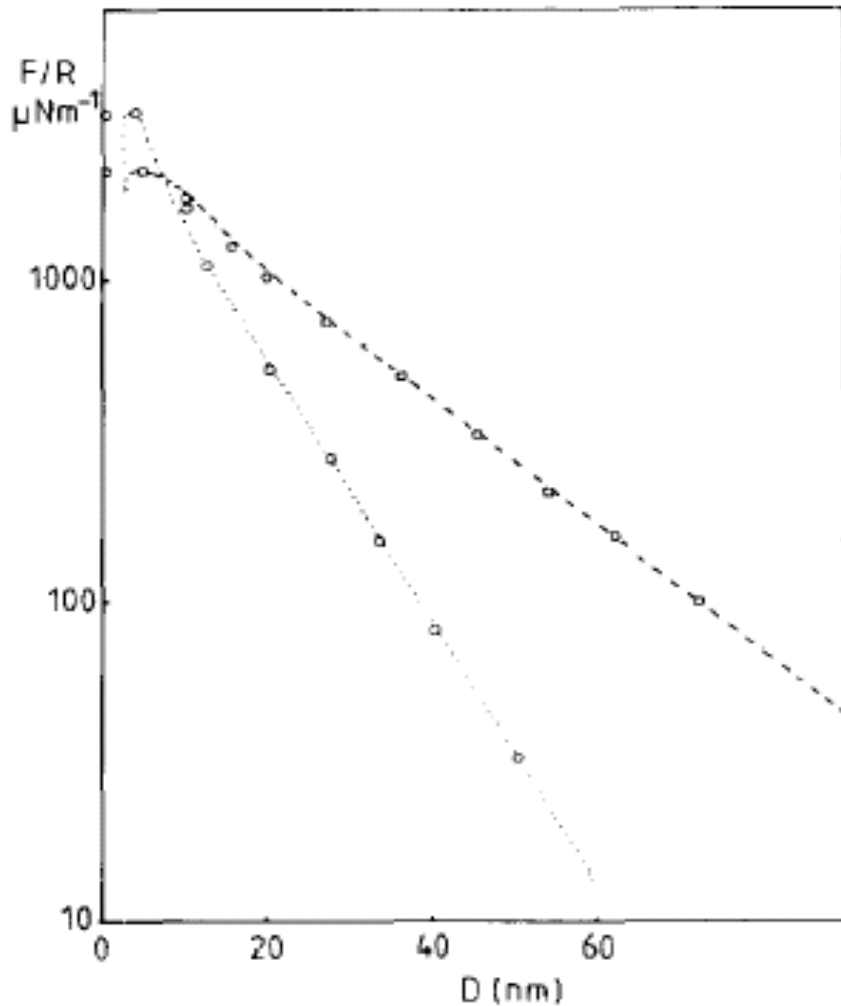


Measurement of particle interactions

- Silicon Nitride Silicon Nitride in Bromonaphthalene

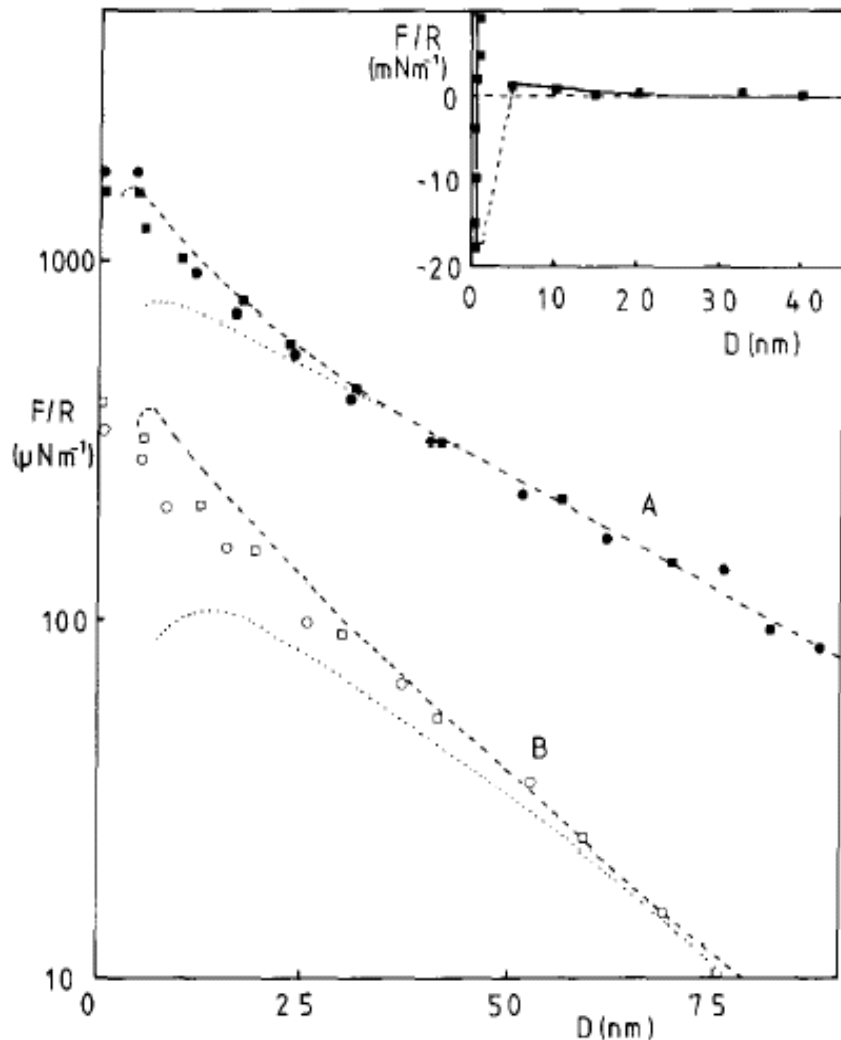


Measurement of particle interactions



The force profile between two curved mica sheets immersed in (i) water (effective electrolyte solution of $1.1 \times 10^{-5} \text{ mol dm}^{-3}$ (\square) and (ii) $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ potassium nitrate solution (\circ). The results have been fitted assuming a surface potential of 110 mV for an interaction at constant surface potential (broken line for water and dotted line for $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ potassium nitrate solution).

Measurement of particle interactions

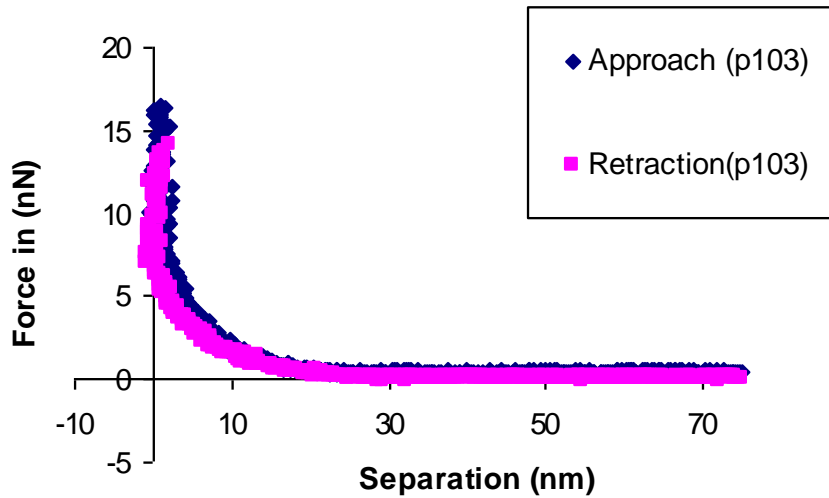


The interaction force profile between two curved mica sheets bearing poly-l-lysine adsorbed from water, molecular weight 4,000 g mol/l, at a solution concentration of 25 mg/l. curve A black symbols. Curve B shows the results obtained when the poly-l-lysine solution was replaced by water.

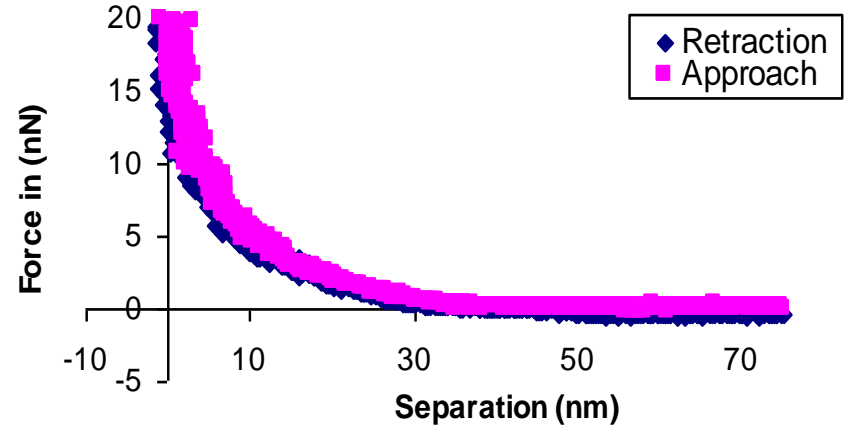
The results for curve A have been fitted (for details see text) assuming a surface potential of 80 mV and an electrolyte concentration of 7.9×10^{-5} mol/l, for constant surface charge (broken line) and constant surface potential (dotted line) interactions. Curve B has been fitted assuming a surface potential of 30 mV and an electrolyte concentration of 1.9×10^{-4} mol/l.

Measurement of particle interactions

PE/P103 IN WATER



PE/P105 IN WATER



Measurement of particle interactions

