GENERAL POLYMER CHEMISTRY
(KJM 5500)

Part II-Macromolecules in solution

Lecture notes

By Bo Nyström

Institute of Chemistry, University of Oslo

Translation by Anna-Lena Kjøniksen

MACROMOLECULES IN SOLUTION

- Macromolecules size, conformation and statistics in dilute solutions

- The thermodynamics of polymer solutions

- Characterization of polymer molecules in dilute polymer solutions

  a) End-group analysis

  b) Osmotic pressure

  c) Light scattering (static)

  d) Ultra centrifugation (equilibrium - and velocity sedimentation)

  e) Diffusion

  f) Viscosity

 g) Gel permeation chromatography (GPC)

- Introduction of the scaling notion

The size, conformation and statistics of random coils

In order to describe the conformation of random coils two parameters are used:

- End-to-end Distance

- Radius of Gyration

With *experimental measurements* one may measure *the radius of gyration*, but not *the end-to-end distance*. The end-to-end distance is though of theoretical interest in connection with polymer statistics.
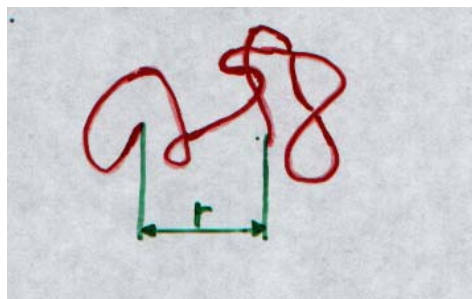
End-to end distance, r, for a conformation of a random coil.

Radius of gyration, R_G: The distance from the center of gravity that all the mass can be gathered into without changing the moment of inertia of the molecule

Moment of inertia $= mass \cdot R_G^2$

Centre of gravity
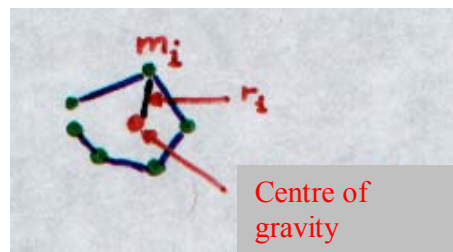
$$R_G^2 = \frac{\sum_i m_i r_i^2}{\sum_i m_i} \qquad (1a)$$

$$\overline{R_G^2} = \frac{\overline{\sum_i m_i r_i^2}}{\sum_i m_i} \qquad (1b)$$

$$\overline{R_G} = \overline{(R_G^2)}^{1/2} = \left(\frac{\overline{\sum_i m_i r_i^2}}{\sum_i m_i}\right)^{1/2} \qquad (1c)$$

If all mass points have an identical mass, M_0:

$$\sum_i m_i r_i^2 = M_0 \sum_i r_i^2 \text{ and } \sum_i m_i = n \cdot M_0$$
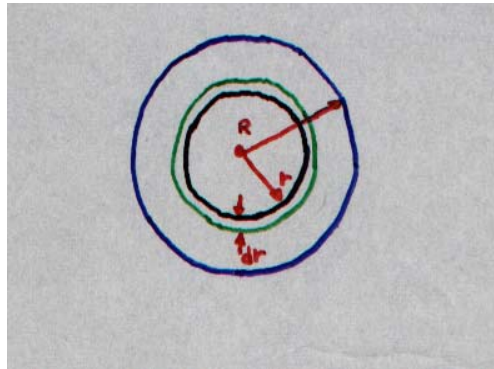
(n = number of monomer units)

From equ. (1c):

$$R_G = \left(\frac{\sum_i \overline{r_i^2}}{n}\right)^{1/2} \qquad (2a)$$

$$R_G = \frac{\left(\sum_i \overline{r_i^2}\right)^{1/2}}{n^{1/2}} \qquad (2b)$$

$$R_G^2 = \frac{\sum_i \overline{r_i^2}}{n} \qquad (2c)$$

The molecular weight dependency of the radius of gyration

Sphere:

$$R_G^2 = \frac{\sum_i r_i^2 m_i}{\sum_i m_i}$$

$$\sum_i r_i^2 \cdot m_i = \int_0^R r^2 dm$$

$$dm = 4 \cdot \pi r^2 \cdot \rho \cdot dr \ (\rho = \frac{m}{V}); \ (V=4\pi r^2 dr)$$

$$\sum_i r_i^2 \cdot m_i = \int_0^R 4 \cdot \pi \cdot r^4 \cdot \rho \cdot dr = \underline{\frac{4 \cdot \pi \cdot \rho \cdot R^5}{5}}$$

$$\langle \int x^n dx = \frac{x^{(n+1)}}{n+1} + const. \rangle$$

$$\sum_i m_i = \int_0^R 4 \cdot \pi \cdot \rho \cdot r^2 \cdot dr = \underline{\frac{4 \cdot \pi \cdot \rho \cdot R^3}{3}}$$

$$R_G^2 = \frac{\frac{4}{5} \cdot \pi \cdot \rho \cdot R^5}{\frac{4}{3} \cdot \pi \cdot \rho \cdot R^3}$$

$$R_G^2 = \frac{3R^2}{5}; \quad R_G = R \cdot \left(\frac{3}{5}\right)^{1/2}$$

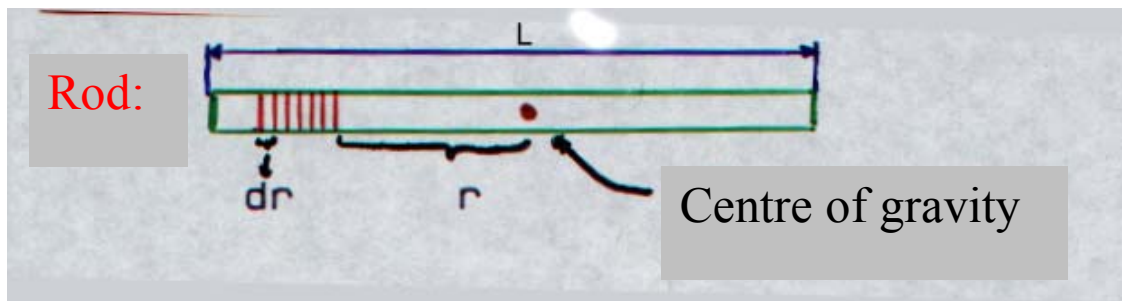$$V(volume) = \bar{v} \cdot \frac{M}{N_A}; \bar{v} = the \ partial \ spesific \ volume$$

$$V = \frac{4 \cdot \pi \cdot R^3}{3}; \ R^3 = \frac{3 \cdot \bar{v} \cdot M}{4 \cdot \pi \cdot N_A}$$

$$R_G = \left(\frac{3}{5}\right)^{1/2} \cdot \left(\frac{3\bar{v}}{4 \cdot \pi \cdot N_A}\right)^{1/3} \cdot M^{1/3}$$

$$\boxed{R_G = const \cdot M^{1/3}} \tag{3}$$

Rod:

The rod has a cross section with an area A.

$$\sum_i r_i^2 m_i = \int_0^{L/2} \rho \cdot r^2 \cdot dr \cdot A = \frac{A \cdot \rho \cdot L^3}{24}$$

$$\sum_i m_i = \int_0^{L/2} A \cdot \rho \cdot dr = \frac{A \cdot \rho \cdot L}{2}$$

$$R_G^2 = \frac{\dfrac{A \cdot \rho \cdot L^3}{24}}{\dfrac{A \cdot \rho \cdot L}{2}} = \frac{L^2}{12}$$

$$R_G = const. \cdot L$$

$$\boxed{R_G = const. \cdot M}$$
<div align="right">(4)</div>

Random coil

Thermodynamic good conditions:

$R_G \propto M^{0.60}$ ("Mean-field" approximation)

$R_g \propto M^{0.588}$ ("Renormalization group theory")

θ-Conditions: $R_g \propto M^{0.50}$

The relation between R_G and the end-to-end distance, r_i, in the molecule

For *linear flexible polymers* the following relation between chain distance (r) and the radius of gyration is valid:

$$\overline{R}_G^2 = \frac{\overline{r^2}}{6} \; ; \quad \left(\overline{r^2}\right)^{1/2} = \left(\overline{6R_G^2}\right)^{1/2} \qquad (5)$$
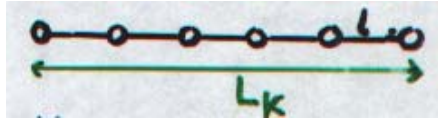
$(\text{---})^{1/2}$ Root-mean-square (r.m.s.)-average.

$$\left(\overline{r^2}\right)^{1/2} = \left[\frac{n_1 r_1^2 + n_2 r_2^2 + \bullet \bullet \bullet n_i r_i^2}{n_1 + n_2 + \bullet \bullet n_i}\right]^{1/2}$$

Models for random coils

1) Chain molecules with a kind of given, locked, rigid structure.

a) *Totally extended chain:*

$$L_K = l \cdot n$$

n = number of bonds; l = bond length; L_K = contour length

b) *Chain with a zigzag structure*

$$r = n \cdot l \cdot \sin\left(\frac{\theta}{2}\right)$$

This chain has a *locked bond angle* that assures that the chain may have *only one conformation*, and that it is *completely rigid*.

2) <u>Chain without restrictions</u>

(bonds that may assume every possible direction with the same probability)

This kind of chain is called *freely joint chain*, and it exhibits *statistics* that is called *random walk*, or drunk mans walk.
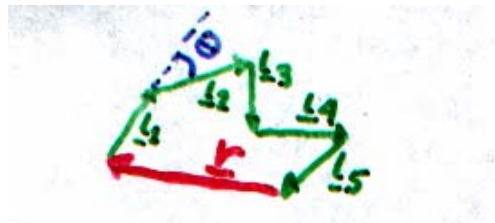
r (the resultant vector) $= (l_1 + l_2 + l_3 + \bullet\bullet\bullet l_n) = \sum\limits_{i=1}^{n} l_i$

$$\overline{r^2} = \overline{r \cdot r} = \left(\sum\limits_{i=1}^{n} \overline{l_i}\right) \cdot \left(\sum\limits_{j=1}^{n} \overline{l_j}\right) = \sum\limits_{i=1}^{n}\sum\limits_{j=1}^{n} \overline{l_i \cdot l_j}$$

$r^2 = (l_1 + l_2 + l_3) \cdot (l_1 + l_2 + l_3) =$
$(l_1 \cdot l_1) + l_1 \cdot l_2 + l_1 \cdot l_3 + l_1 \cdot l_2 +$
$(l_2 \cdot l_2) + l_2 \cdot l_3 + l_1 \cdot l_3 + l_2 \cdot l_3 + (l_3 \cdot l_3)$

(   ) represents i=j

When $i = j; l_i \cdot l_i = l^2$ (*l* is the lenght of the vector)

If we have n monomers in the chain, we have (n-1)≈n vectors. We assume that all bonds is of the same length l and multiply out all i=j, we get the square-average of the *end-to-end-distance*

$$\langle r^2 \rangle = n \cdot l^2 + \sum_{i=1}^{n}\sum_{j=1}^{n}\langle l_i \cdot l_j \rangle \quad (i \neq j) \tag{6}$$

For $l_i \cdot l_j$ with $i \neq j$, we get:

$$\langle l_i \cdot l_j \rangle = l^2 \cdot \langle \cos\theta \rangle;$$ where θ is the angle between the vectors.
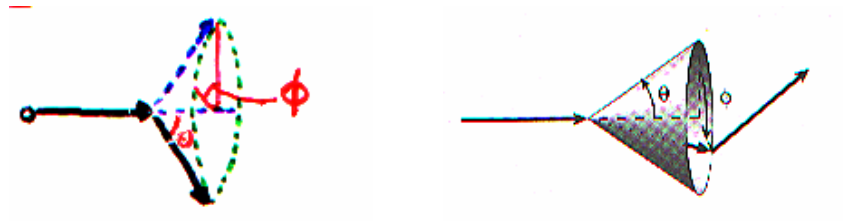
For a random coil all values of θ are equally probable

$$\langle \cos\theta \rangle = 0; \quad \langle r^2 \rangle = n \cdot l^2$$

$$\boxed{\langle r \rangle = n^{1/2} \cdot l} \tag{7}$$

For a *rod like particle* the equivalent expression is:

$$r = n \cdot l \qquad\qquad\qquad (8)$$

3) Free rotation, fixed bond angle

In this case one lets the *bond angle* be set at a *fixed value*. One allows *free rotation around the bond*.

In this case, the last part of the equ. (6) *is not zero* due to the *fixed bond angle*.

$$\boxed{\langle r^2 \rangle = n \cdot l^2 \cdot \frac{1 + \cos\theta}{1 - \cos\theta}} \qquad\qquad (9)$$

(This locking of the bond angle gives an increase of $\langle r \rangle$).

Equ. (8) and (9) is only valid when the end-to-end distance exhibits a Gauss distribution.

If we identify this bond angle with the tetraeder-angle $(\theta = 109^o)$ we get equ. (9):

$$\langle r^2 \rangle = 2.00 \cdot n \cdot l^2 \qquad (10)$$

If we compare this result with the experimental result for *polyethylene*:

$$\langle r^2 \rangle = (6.7 \pm 0.3) \cdot n \cdot l^2$$

we observe that this *model* gives too *small values*.

4) Hindered rotation

We will now take into consideration a fact that is often the case for polymer chains, namely *when the rotation around the single bonds is not free*.

For a complete description of the conformation of a model chain, we have to have information of both the *bond angle* (θ) and the *rotation angle* (ϕ) (torsion angle).

$$\langle r^2 \rangle = n \cdot l^2 \cdot \frac{1 + \cos\theta}{1 - \cos\theta} \cdot \frac{1 + \langle \cos\phi \rangle}{1 - \langle \cos\phi \rangle} \qquad (11)$$

$\langle \cos\phi \rangle = 0$ (free rotation) ; $\langle \cos\phi \rangle \neq 0$ (hindered rotation)

Equ. (11) takes into account trans- and gauche-conformations. If the gauche- and trans-conformations have the same energy: $\cos\phi = 0$

Real polymer chains (short-range interactions)

The end-to-end distance, r, for a polymer chain with a fixed bound angle, θ, and the rotation angle, ϕ, may be written as:

$$\langle r^2 \rangle = n \cdot l^2 \cdot \frac{1+\cos\theta}{1-\cos\theta} \cdot \frac{1+\langle\cos\phi\rangle}{1-\langle\cos\phi\rangle}$$

Let us now replace the real bound length l with a fictive bound length, β, which is called the effective bound length:

$$\langle r^2 \rangle = n \cdot \beta^2$$

The ratio $\dfrac{\beta}{l}$ is a measure of the stiffness of the

polymer chain.

$$C = \dfrac{\beta^2}{l^2} \text{ : the characteristic ratio.}$$

Ex.:

Polymer	C
Polyethylene	6.8
Polystyrene	9.9
Polyethylene oxide	4.1
Polybuthadiene	4.8

Definition of the Kuhn length l_{ku}

We may generally describe a *statistic chain molecule*

with the aid of the concept *equivalent statistic*

segment. In this case we imagine that instead of

contemplating a chain that consists of real segments

with a hindered rotation around the bonds and fixed

bond angles, we make a *hypothetical statistic chain*

with *the same chain length* and *the same end-to-end distance* as the real chain. (n=30, N_k=5)
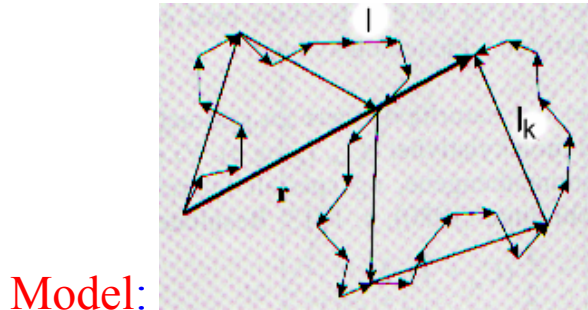
Model:

We got the following equation: $\langle r^2 \rangle = Cnl^2$

By using the *Kuhn-model,* we get

$$\langle r^2 \rangle = N_{ku} \cdot l_{ku}^2$$

For a *fully outstretched chain,* we get the *contour length* L_k

$$L_k = n \cdot l$$

For the *hypothetical chain*

$$L_k = N_{ku} \cdot l_{ku}$$

We got: $n \cdot l = N_{ku} \cdot l_{ku}$

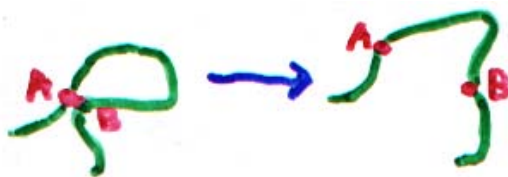$$l_{ku} \cdot n \cdot l = N_{ku} \cdot l_{ku}^2 = C \cdot n \cdot l^2$$

$$\boxed{l_{ku} = C \cdot l}$$

$$\boxed{N_{ku} = \frac{n}{C}}$$

We see from these two equations that the stiffer the molecule, the longer is the Kuhn-segment, while there will be a smaller number of Kuhn-segments.

Polymer chains and excluded volume effects

("long-range"-interactions)

Non-perturbed Chain   Excluded Volume Effect
(θ-conditions)   (Good conditions)

$$\langle r^2 \rangle = \alpha^2 \cdot \beta^2 \cdot n$$

$$\alpha = \frac{\langle r^2 \rangle^{1/2}}{\langle r^2 \rangle_0^{1/2}}$$

α = expansion coefficient.

$\langle r^2 \rangle_0^{1/2}$ = the ideal conformation or the non-perturbed

dimension.

Polymer molecules have the dimension $\langle r^2 \rangle_0^{1/2}$ in a θ-

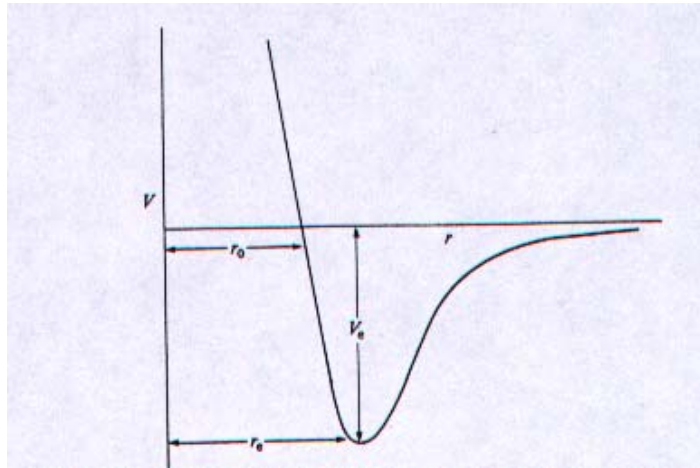solvent (ideal solvent).

Thermodynamic good solvents: $\alpha > 1$

θ-solvents: $\alpha = 1$

Thermodynamic poor solvents: $\alpha < 1$

Interactions and size of chain molecules at different thermodynamic conditions.

Potential curve

Lennard-Jones

$$\text{potential:} V(r) = 4V_e\left[\left(\frac{r}{r_0}\right)^{-12} - \left(\frac{r}{r_0}\right)^{-6}\right]$$

1. At *short distances repulsion* between the monomers

2. At *long distances attractive interactions* between the monomers

$$R_G \propto M^{1/3} \qquad R_G \propto M^{1/2} \qquad R_G \propto M^{0.6}$$

"Globule" attractive mon.-mon. interactions. $\alpha < 1; v < 0$ v is the excluded volume parameter	The attractive and repulsive interactions compensate each other. Ideal chain $\alpha = 1; v = 0$ Gaussian statistics	Repulsive interactions leads to an expansion of the chain. $\alpha > 1; v > 0$ Excluded volume statistics

Look at how the *thermodynamic conditions* change with *temperature*. (e.g. Polystyrene/cyclohexane; θ-temperature 35 °C)
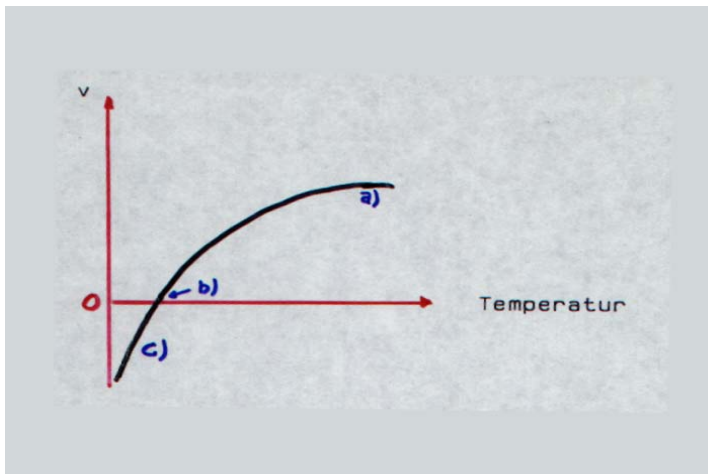
a) Good conditions
b) θ-conditions
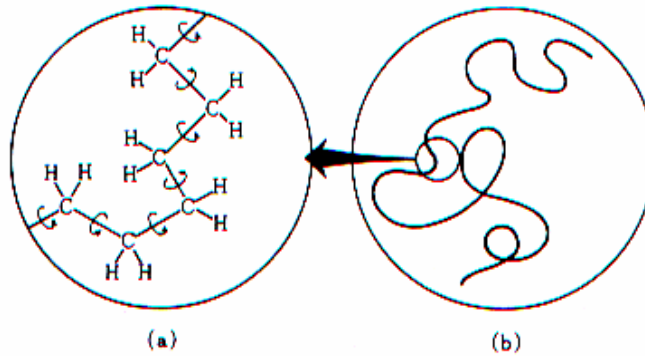c) "Collapse" region

$$v = a^3(1-2\varepsilon_1)$$

v = Excluded volume parameter

a = Monomer radius

ε_1 = Flory-Huggins interaction parameter

At θ-conditions, v = 0 and ε_1 = 0.50.
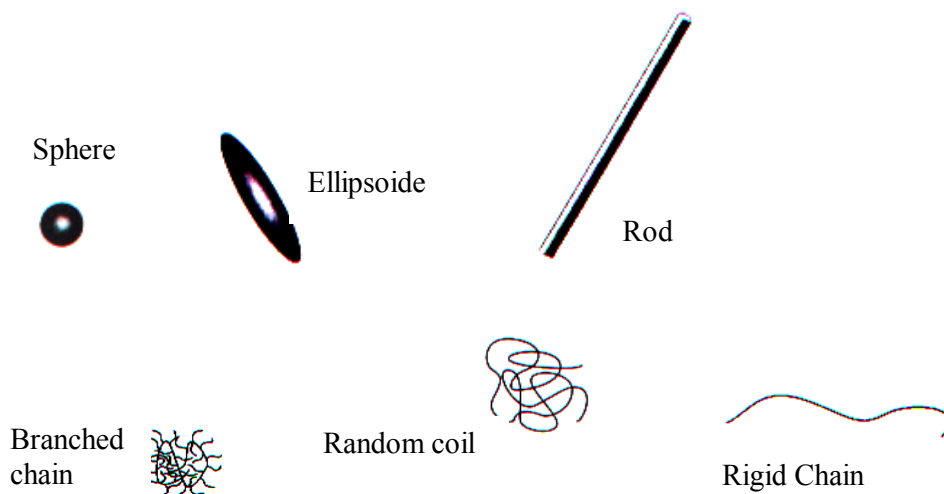
Microscopic structure and macromolecular conformations

(a)   (b)

a) Microscopic structure of PE

b) Macroscopic conformation of PE

Different conformations of polymers.

Sphere

Ellipsoide

Rod

Branched chain

Random coil

Rigid Chain

$$g = \frac{\langle R_G^2 \rangle (\text{branched})}{\langle R_G^2 \rangle (\text{linear})}; \; g < 0.9$$

Ex.: Star shaped polymer with function = 6

$$g(\text{star}) = \frac{3f - 2}{f^2} = 0.4 \, (f = 6)$$

The thermodynamic properties of polymer solutions

Thermodynamic functions for mixtures:

The total Gibbs energy for a solution: $G = \sum_i n_i \cdot \mu_i$

n_i = number of mol of the component i

μ_i = chemical potential of the component i

Change in Gibbs molar energy for a *mixture*:

$$\Delta G_m = \sum_i n_i \left(\mu_i - \mu_i^0 \right) = G - \sum_i n_i \mu_i^0$$

$\mu_i^0 =$ chemical potential in the standard condition (pure substance).

In the same way *the change in mixing enthalpy* is defined:

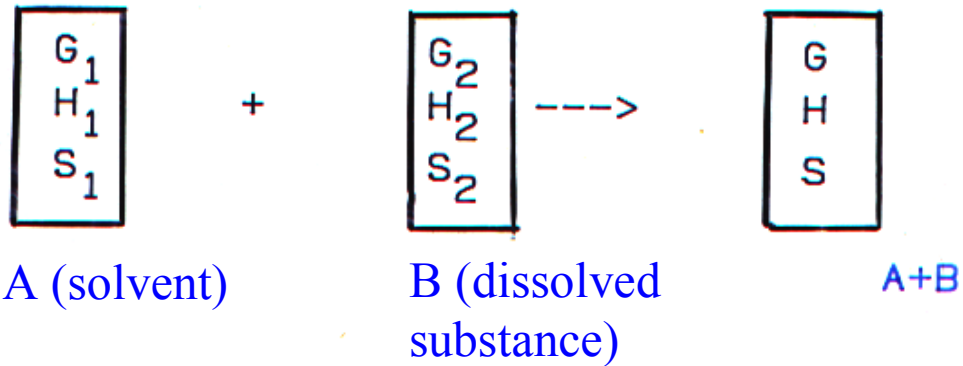$$\Delta H_m = \sum_i n_i \left(H_i - H_i^0 \right) = H - \sum_i n_i H_i^0$$

and *mixing entropy:*

$$\Delta S_m = \sum_i n_i \left(S_i - S_i^0 \right) = S - \sum_i n_i S_i^0$$

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (\text{Gibbs - Helmholz})$$

Ex.:   Look at a *two-component system*

$\Delta G_m = G - (G_1 + G_2); \ \Delta H_m = H - (H_1 + H_2)$

$\Delta S_m = S - (S_1 + S_2)$

These quantities is related in the usual way:

$$\boxed{\Delta G_m = \Delta H_m - T \cdot \Delta S_m}$$ (12)

Partial molar and partial specific quantities

Intensive quantities: Quantities that are independent of the size of the system (e.g. temperature and pressure).

Extensive quantities: Quantities that are dependent of the size of the system (e.g. weight, volume, Gibbs energy, enthalpy and entropy).

Partial molar quantities

$$\overline{Y}_i = \left(\frac{\partial Y}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Partial molar volume:

$$\overline{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{i\neq j}}$$

$$\overline{V}_1 = \left(\frac{\partial V}{\partial n_1}\right)_{T,P} \qquad\qquad (13)$$

Partial molar Gibbs energy:

$$\mu_i - \mu_i^0 = \overline{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j \neq i}}$$

$$\boxed{\left(\frac{\partial G}{\partial n_1}\right)_{T,P} = \mu_1 - \mu_1^0 = RT \ln X_1 = -\Pi \cdot \overline{V}_1 \; ; \; \Pi = \text{osmotic pressure}}$$

(14)

$$X_1 = \frac{n_1}{n_1 + n_2} \; ; \; \text{mol fraction}$$

Partial specific quantities:

$$\bar{y}_i = \left(\frac{\partial Y}{\partial g_i}\right)_{T,P,g_{j\neq i}}$$
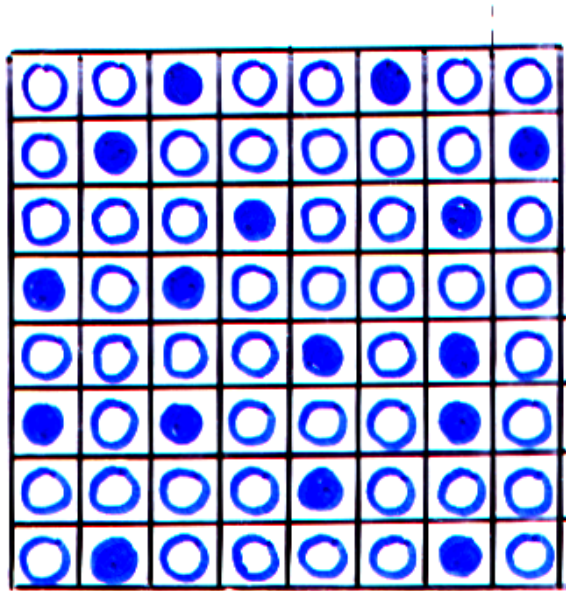
g_i is the weight of component i.

Partial specific volume:

$$\bar{v}_i = \left(\frac{\partial V}{\partial g_i}\right)_{T,P,g_{j\neq i}}$$

The relation between partial molar and partial specific

quantities is:

$$\bar{v}_i = \frac{\bar{V}_i}{M_i}; \text{ where } M_i \text{ is the molecular weight of}$$
component i

Calculation of the ideal statistic contribution to ΔS_m

o Solvent   :● Dissolved substance

$$S = k \cdot \ln\Omega \qquad\qquad (15)$$

Ω = Number of different micro conditions

k = Boltzman's constant

This equation gives the basis for a *molecular understanding of macroscopic conditions*

$N_0 = N_1 + N_2$

N_0 = total number of lattice positions
N_1 = number of solvent molecules
N_2 = number of molecules of the dissolved substance

There are N_0 ways to arrange the first molecule, and

N_0-1 ways to arrange the second molecule in the

lattice. There are $N_0(N_0$-1$)$ ways to arrange the two

first molecules etc.

$$\Omega' = N_0(N_0 - 1) \cdot (N_0 - 2) \cdot (N_0 - 3) \cdots = N_0!$$

We have to correct Ω' with the number of ways N_1

and N_2 molecules may be permutated

$$\Omega = \frac{N_0!}{N_1! \cdot N_2!} \qquad\qquad (16)$$

For the *pure* components:

$$\Omega_1 = \Omega_2 = \frac{N_1!}{N_1!} = \frac{N_2!}{N_2!} = 1$$

$N_0 = 3$; $N_1 = 1$; $N_2 = 2$

1 molecule A and 2 molecules B

$$\Omega = \frac{1 \cdot 2 \cdot 3}{1 \cdot 1 \cdot 2} = 3 \; ; \text{ABB; BAB; BBA}$$

Ex 2 $N_0 = 4$; $N_1 = 2$; $N_2 = 2$

2 molecules A and 2 molecules B

$$\Omega = \frac{1 \cdot 2 \cdot 3 \cdot 4}{1 \cdot 2 \cdot 1 \cdot 2} = 6 \; ; \text{ AABB; ABAB; BAAB; BABA;}$$

ABBA; BBAA

$$\Delta S_m = S - S_1 - S_2$$

$$\Delta S_m = k \cdot \ln \Omega - k \cdot \ln \Omega_1 - k \cdot \ln \Omega_2$$

From combination of equ. (15) and (16):

$$\Delta S_m = k(\ln N_0! - \ln N_1! - \ln N_2!) \qquad (17)$$

Since all N are *large numbers*, we may use *Stirlings approximation*.

$$\ln N! = N \cdot \ln N - N$$

$$\Delta S_m = k \cdot \left[(N_1 + N_2) \cdot \ln(N_1 + N_2) - (N_1 + N_2) - \right.$$

$$\left. - N_1 \cdot \ln N_1 + N_1 - N_2 \cdot \ln N_2 + N_2 \right]$$

$$\Delta S_m = k \cdot \left[N_1 \cdot \ln(N_1 + N_2) + N_2 \cdot \ln(N_1 + N_2) - \right.$$

$$\left. - N_1 - N_2 - N_1 \cdot \ln N_1 + N_1 - N_2 \cdot \ln N_2 + N_2 \right]$$

$$\Delta S_m = -k \cdot \left[- N_1 \cdot \ln(N_1 + N_2) - N_2 \cdot \ln(N_1 + N_2) + \right.$$

$$\left. + N_1 \cdot \ln N_1 + N_2 \cdot \ln N_2 \right]$$

$$\Delta S_m = -k \left[N_1 \ln \frac{N_1}{N_1 + N_2} + N_2 \ln \frac{N_2}{N_1 + N_2} \right] \quad (18)$$

$$R = N_A \cdot k; \; N_i = N_A \cdot n_i; \; X_i = \frac{n_i}{\sum_i n_i}$$

$$X_1 = \frac{n_1}{n_1 + n_2}; \; X_2 = \frac{n_2}{n_1 + n_2}$$

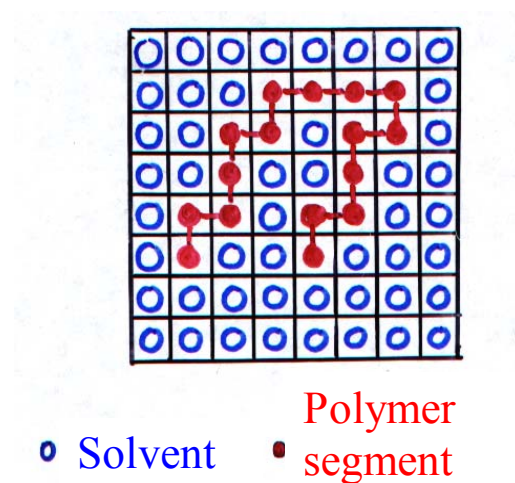$$\boxed{\Delta S_m = -R(n_1 \ln X_1 + n_2 \cdot \ln X_2)} \quad (19)$$

If we assume that *the solution is ideal,* then $\Delta H_m = 0$.

From equ. (12):

$$\boxed{\Delta G_m = R \cdot T \cdot (n_1 \cdot \ln X_1 + n_2 \cdot \ln X_2)} \qquad (20)$$

Flory-Huggins model *("mean-field" consideration)*

for binary polymer solutions

In this case, the x chain segments are coupled together with each other. Except from this, the deduction will be analog with the earlier case.

o Solvent   • Polymer segment

$$N_0 = N_1 + x \cdot N_2$$

$$\Delta S_m = -k\left[N_1 \cdot \ln \frac{N_1}{N_1 + x \cdot N_2} + N_2 \cdot \ln \frac{xN_2}{N_1 + x \cdot N_2}\right] \quad (21)$$

Compare with equ. (18).

The volume fraction for the solvent (Φ_1) and for the polymer (Φ_2).

$$\Phi_1 = \frac{N_1}{N_1 + x \cdot N_2}; \ \Phi_2 = \frac{x \cdot N_2}{N_1 + x \cdot N_2}$$

$$\Delta S_m = -R\left(n_1 \cdot \ln \Phi_1 + n_2 \cdot \ln \Phi_2\right) \qquad (22)$$

It is important to point out *equ. (22)* only represent *the configuration entropy of the mixture.*

In addition there may exist *an other type of entropy* that is due to *specific interactions* between *polymer- and solvent molecules*.

In *Flory-Huggins theory* we assume that $\partial H \neq 0$ because the polymer-solvent interaction energies are different from the polymer-polymer and solvent-solvent interaction energies.

Mixing enthalpy for polymer and solvent

Type of contacts		Interaction energies
Solvent-solvent	(1,1)	w_{11}
Polymer-polymer	(2,2)	w_{22}
Solvent-polymer	(1,2)	w_{12}

The dissolving process may be written as the change of these contacts:

$$(1,1)\cdot 1/2 + (2,2)\cdot 1/2 \rightarrow (1,2)$$

The difference in energy, Δ_w, is:

$$\Delta_w = w_{12} - (w_{11} + w_{22})\cdot 1/2$$

If the average number of 1,2 contacts in the solution is $P_{1,2}$ (over all lattice configurations), *the mixing enthalpy is*:

$$\Delta H_m = \Delta w \cdot P_{1,2}$$
$$P_{1,2} = x \cdot N_2 \cdot \Phi_1 \cdot Z$$
$$\Delta H_m = x \cdot N_2 \cdot \Phi_1 \cdot Z \cdot \Delta w$$

Φ_1 = the probability of 1,2 contacts

Z = the coordination number for a certain lattice position

From the definition of volume fraction, we get (by dividing these with each other):

$$x \cdot N_2 \cdot \Phi_1 = N_1 \cdot \Phi_2 \,; \; \Delta H_m = N_1 \cdot \Phi_2 \cdot Z \cdot \Delta w$$

Let us now define a new parameter ε_1 (Flory-Huggins parameter) that expresses *polymer-solvent interactions*:

$$Z \cdot \Delta w = \varepsilon_1 \cdot k \cdot T; \qquad \varepsilon_1 = \frac{Z \cdot \Delta w}{k \cdot T}$$

$$\boxed{\Delta H_m = N_1 \cdot \Phi_2 \cdot \varepsilon_1 k \cdot T = n_1 \Phi_2 \cdot \varepsilon_1 \cdot R \cdot T} \qquad (23)$$

We now got equations for ΔS_m (equ. 22) and ΔH_m:

$$\Delta G_m = R \cdot T\left(n_1 \cdot \Phi_2 \cdot \varepsilon_1 + n_1 \ln \Phi_1 + n_2 \ln \Phi_2\right) \qquad (24)$$

This equation transforms into equ. (20) when

$x = 1$ and $\varepsilon_1 = 0$.

The use of Flory-Huggins theory to calculate the partial molar Gibbs energy

$$\Delta \overline{G}_1 = \left(\frac{\partial(\Delta G_m)}{\partial n_1}\right)_{T,P} ; \text{ diff.equ. (24)}$$

$$\Delta \overline{G}_1 = RT \cdot \left[\left(\frac{\partial \Phi_1}{\partial n_1}\right)_{n_2} \cdot \frac{n_1}{\Phi_1} + \ln \Phi_1 + \left(\frac{\partial \Phi_2}{\partial n_1}\right)_{n_2} \cdot \frac{n_2}{\Phi_2} + \varepsilon_1 \cdot \Phi_2 + \varepsilon_1 \cdot n_1 \cdot \left(\frac{\partial \Phi_2}{\partial n_1}\right)_{n_2}\right]$$

$$(25)$$

Use $\Phi_1 + \Phi_2 = 1$ and differentiate:

$$\left(\frac{d}{dx}(u \cdot v) = u \cdot \frac{dv}{dx} + v\frac{du}{dx}\right)$$

$$\left(\frac{d}{dx}\left(\frac{u}{v}\right) = \frac{v(du/dx) - u(dv/dx)}{v^2}\right)$$

$$\Phi_1 = \frac{n_1}{n_1 + x \cdot n_2}; \; \Phi_2 = \frac{x \cdot n_2}{n_1 + x \cdot n_2}$$

$$\Delta\overline{G}_1 = R \cdot T \cdot \left[\ln(1 - \Phi_2) + \left(1 - \frac{1}{x}\right) \cdot \Phi_2 + \varepsilon_1 \cdot \Phi_2^2\right] \quad (26)$$

For *dilute solutions*: $\Phi_2 \ll 1$. We may use a polynomial approximation (Mac-Laurin)

$$\ln(1 - \Phi_2) \approx -\Phi_2 - \frac{\Phi_2^2}{2} - \frac{\Phi_2^3}{3} - \dots$$

$$\Delta\overline{G}_1 = R \cdot T \cdot \left[-\frac{\Phi_2}{x} - \left(\frac{1}{2} - \varepsilon_1\right) \cdot \Phi_2^2 - \frac{\Phi_2^3}{3} - \dots\right] (26a)$$

(see equation 14)

44

$$-\pi \cdot \overline{V}_1 = \mu_1 - \mu_0 = R \cdot T \cdot \left[-\frac{\Phi_2}{x} - \left(\frac{1}{2} - \varepsilon_1\right) \cdot \Phi_2^2 - \frac{\Phi_2^3}{3} \right]$$

When

$$x = \frac{\overline{V}_2}{\overline{V}_1}; \Phi_2 = n_2 \cdot \frac{V_2}{n_1 \cdot V_1 + n_2 \cdot V_2} = c \cdot \frac{\overline{V}_2}{M_2} \quad c = \text{cons.}\left(\frac{\text{mass}}{V}\right)$$

$$v_i = \frac{\overline{V}_i}{M_i} = \frac{1}{\rho_i} (\rho_i = \text{density})$$

$$\boxed{-\pi = \left[-\frac{c \cdot \overline{V}_1}{M_2} - \left(\frac{1}{2} - \varepsilon_1\right) \cdot \frac{c^2 \overline{V}_2^2}{M_2^2} - \cdots \right] \frac{R \cdot T}{\overline{V}_1}} \qquad (27)$$

$$A_2 = \frac{\left(\frac{1}{2} - \varepsilon_1\right) \cdot M_2^2 \cdot \rho_1}{\rho_2^2 \cdot M_2^2 \cdot M_1}$$

$$A_2 = \frac{\left(\frac{1}{2} - \varepsilon_1\right) \cdot \rho_1}{\rho_2^2 \cdot M_1}$$

A_2 is the second virial coefficient.

$$\Pi = c \cdot R \cdot T\left(\frac{1}{M_2} + A_2 c + ...\right) \qquad (27a)$$

Discussion of Flory-Huggins interaction parameter

- ε_1 is often dependent of the polymer concentration

- ε_1 is also temperature dependent

- The experimental value of ε_1 often diverges from the theoretical value. This is related to the fact that the *Flory-Huggins parameter,* ε_1, consists of both an *enthalpy part* and an *entropy part.*

$\varepsilon = \varepsilon_H + \varepsilon_S$; ε_S is constant

and

$\varepsilon_H = -T \cdot \dfrac{\partial \varepsilon}{\partial T}$; the enthalpy is dependent of T

Flory-Krigbaum theory of dilute polymer solutions
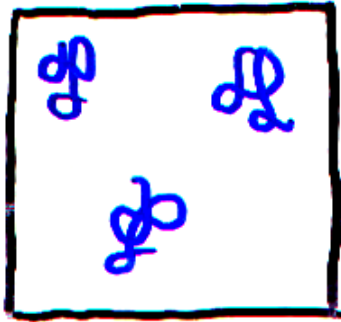
Dilute Solution

The factor $\dfrac{1}{2} - \varepsilon_1$ may be viewed as a measure of the

deviation from the *properties* of an *ideal solution*.

This contribution to Gibbs molar energy is called

ΔG_1^E, and may consist of both *enthalpy- and entropy*

components:

$$\Delta \overline{G}_1^{E} = R \cdot T \cdot (\psi_1 - \tau_1) \cdot \Phi_2^2 \qquad (28)$$

$E = $ "excess"
$\tau_1 = $ enthalpy parameter
$\psi_1 = $ entropy parameter

$$\boxed{-\Delta G_1^E = -\Delta H_1^E + T \cdot \Delta S_1^E} \qquad (29)$$

$$\boxed{\Delta H_1^E = R \cdot T \cdot \tau_1 \cdot \Phi_2^2}$$ (30)

$$\boxed{\Delta S_1^E = R \cdot \psi_1 \cdot \Phi_2^2}$$ (31)

$$(\psi_1 - \tau_1) = \frac{1}{2} - \varepsilon_1$$

$$\Delta G_1^E = 0 \rightarrow \theta \cdot \Delta S_1^E = \Delta H_1^E$$

$$\theta \cdot R \cdot \psi_1 \cdot \Phi_2^2 = R \cdot T \cdot \tau_1 \cdot \Phi_2^2$$

$$\theta = \frac{T \cdot \tau_1}{\psi_1}$$

$$\boxed{\psi_1 - \tau_1 = \psi_1 \cdot \left(1 - \frac{\theta}{T}\right) = \frac{1}{2} - \varepsilon_1}$$ (32)

One may express the expansion factor α in terms of

the Flory-temperature θ

$$\boxed{\alpha^5 - \alpha^3 = 2 \cdot C_m \cdot \psi_1 \cdot \left(1 - \frac{\theta}{T}\right) \cdot M^{1/2}}$$ (33)

C_m is a constant.

We see that at the θ-temperature (T=θ), α=1. For high

molecular weights, equ 33 gives $\alpha^5 \propto M^{1/2} \Rightarrow$

$$\alpha \propto M^{0.1} \quad \alpha = \frac{R_G}{R_{G,\theta}} \propto \frac{R_G}{M^{0.5}} ; R_G(good) \propto M^{0.6}$$

Phase equilibriums

Let us consider a *two-component system* that consists

of a polymer dissolved in a thermodynamic *poor*

solvent that gets *better with increasing temperature*.

x_2 **(mol fraction pol.)**
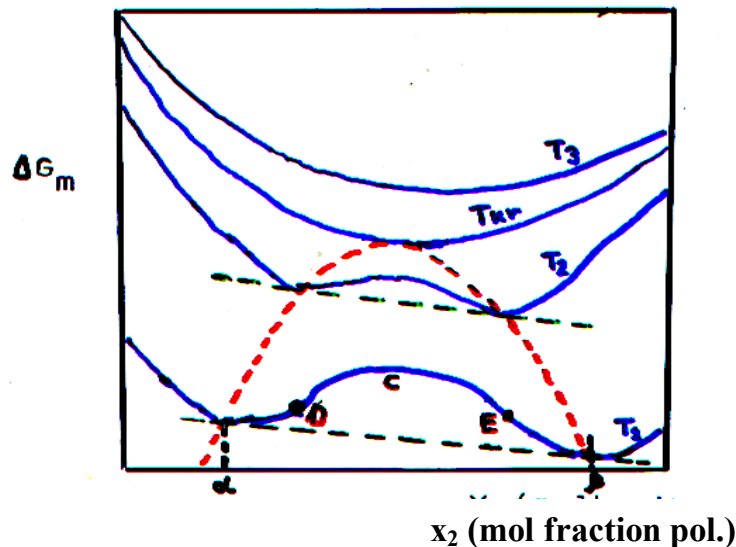
Two phases α and β shares a *common tangent*. A *homogenous phase* is *stabile* if $X_2 < α$ or $X_2 > β$.

Thermodynamically *unstable* in the area $α \leq X_2 \leq β$. At T_3 one has a system that is *completely mixable*.

T_{kr} = *critical temperature* for solubility.

D and E represents *inflection points* on the curve.

The striped red curve (the turbidity curve) represents the *heterogeneous two-phase region*.

For the inflection points D and E the following mathematical relation is valid:

$$\frac{\partial^2 (\Delta G_m)}{\partial \Phi_2^2} = 0 \quad \text{and} \quad \frac{\partial^3 (\Delta G_m)}{\partial \Phi_2^3} = 0$$

because D and E converge in the critical point. We have used volume fraction, but the same is valid if one uses mol fraction X.

$$\Delta G_i = \frac{\partial (\Delta G_m)}{\partial \Phi_i} = \mu_i; \quad \frac{\partial \mu_1}{\partial \Phi_2} = 0 \quad \text{and} \quad \frac{\partial^2 \mu_1}{\partial \Phi_2^2} = 0$$

We got: (see equ. 26)

$$\frac{\mu_1 - \mu_0}{RT} = \ln(1 - \Phi_2) + (1 - \frac{1}{x}) \cdot \Phi_2 + \varepsilon_1 \Phi_2^2$$

$$\frac{\partial \mu_1}{\partial \Phi_2} = -\frac{1}{1 - \Phi_{2,c}} + (1 - \frac{1}{x}) + 2 \cdot \varepsilon_{1,c} \Phi_{2,c} = 0$$

$$\frac{\partial^2 \mu_1}{\partial \Phi_2^2} = \frac{(-1) \cdot (-1)}{(1 - \Phi_{2,c})^2} - 2 \cdot \varepsilon_{1,c} = 0$$

We may write the equations above in the following way:

$$\frac{1}{1-\Phi_{2,c}} - (1-\frac{1}{x}) - 2\cdot\varepsilon_{1,c}\Phi_{2,c} = 0 \qquad\qquad \text{(a)}$$

$$\frac{1}{(1-\Phi_{2,c})^2} - 2\cdot\varepsilon_{1,c} = 0 \qquad\qquad \text{(b)}$$

By combining equation (a) and (b), we can derive the following relations:

$$\Phi_{2,c} = \frac{1}{1+x^{1/2}}$$

$$\varepsilon_{1,c} = \frac{1}{2}\cdot\left(1+\frac{1}{x^{1/2}}\right)^2 = \frac{1}{2} + \frac{1}{2x} + \frac{1}{x^{1/2}}$$

When $\quad x \rightarrow \infty;\ \Phi_{2,c} = \dfrac{1}{x^{1/2}}$ and $\varepsilon_{1,c} = \dfrac{1}{2}$

From equ. (32): $\quad \psi_1 - \tau_1 = \psi_1 \cdot \left(1 - \dfrac{\theta}{T}\right) = \dfrac{1}{2} - \varepsilon_1$

$$\psi_1 \cdot \left(1 - \frac{\theta}{T_c}\right) = \frac{1}{2} - \frac{1}{2} - \frac{1}{2x} - \frac{1}{x^{1/2}}$$

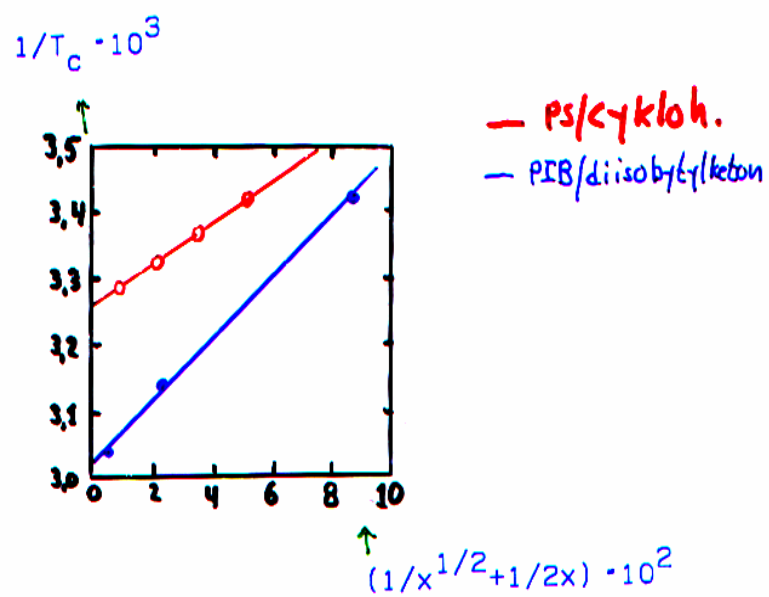$$\frac{\theta}{T_c} = 1 + \frac{\dfrac{1}{2x} + \dfrac{1}{x^{1/2}}}{\psi_1}$$

$$\boxed{\frac{1}{T_c} = \frac{1}{\theta} \cdot \left(1 + \frac{\dfrac{1}{2x} + \dfrac{1}{x^{1/2}}}{\psi_1}\right)} \qquad (34)$$

When $\quad x \to \infty, \; T_c = \theta$

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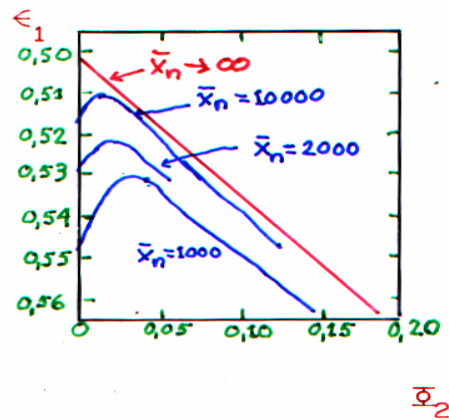
$$\frac{1}{T_c} = \frac{1}{\theta} \cdot \left[1 + \frac{\dfrac{1}{2x} + \dfrac{1}{x^{1/2}}}{\Psi_1} \right]$$

Plot of $\dfrac{1}{T_c}$ against $\dfrac{1}{x^{1/2}} + \dfrac{1}{2x}$

Upper critical solution temperature (UCST) and Lower critical solution temperature (LCST)

Illustration with example:

Temperatur (K)

463
453 ———————— 37000
443 ———————— 97000
        200000
433 ———————— 400000
        M = 2,7·10^6   **LCST**

UCST
        M ≈ 2,7·10^6
283 ———————— 400000
        200000
273 ———————— 97000
263 ———————— 37000

0,05 0,10 0,15 0,20 0,25 0,30

PS/Cyklopentan

Θ = 293 K

w$_2$(weight fraction)
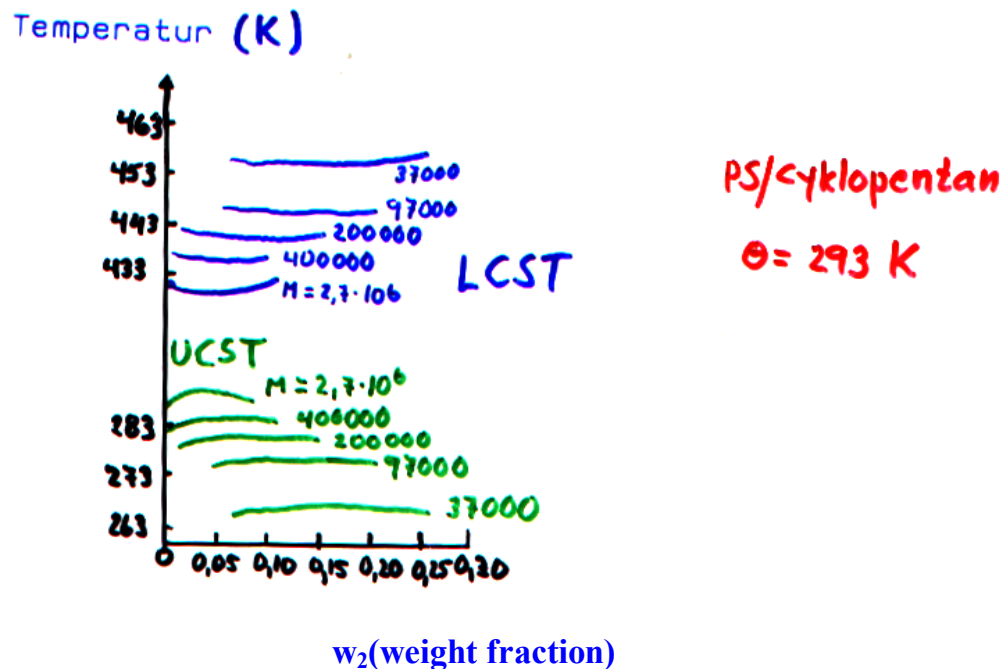
Characterizing polymer solutions

Analyses of end groups:

• Estimation of the number of end groups. If the chemical structure of the molecule is known, $\overline{M}_n$ can be determined.

Methods that are used for analyses:

a) Chemical: *Titration methods* is often used (carboxyl, hydroxyl, amino groups) (polyester and polyamides)

b) Radio chemical: Introduction of radioactive groups under polymerization in order to measure the radioactivity of the produced polymer

c) Spectroscopic: (IR and UV)

These methods may be used together with e.g. *osmometry* in order to gain information of *polymerization mechanisms* and *branching reactions*.

Osmotic pressure (Π)

Semi permeable membrane
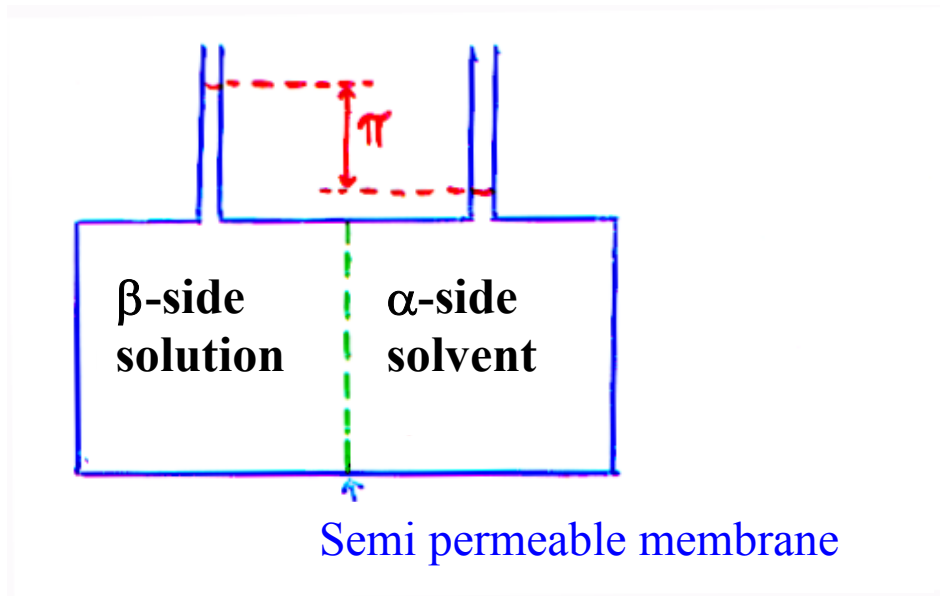
α-side: Pure solvent; component 1

β-side: Polymer solution; polymer (component 2)

+ solvent (component 1)

At start: $\mu_1^\alpha = \mu_1^0$ (1 atm)

$\mu_1^\beta < \mu_1^0$

At equilibrium: $\mu_1^\alpha = \mu_1^\beta + \int_{P_0}^{P} \left(\frac{\partial \mu_1}{\partial P} \right)_T \cdot \partial P$

From *thermodynamics*:

$$\left(\frac{\partial \mu_1}{\partial P}\right)_{T,n_1 n_2} = \overline{V}_1 \quad \text{(mol.vol. of solvent)}$$

$$\mu_1^{\alpha} - \mu_1^{\beta} = V_1(P - P_0)$$

$$\Delta\overline{G}_1 = \mu_1^{\beta} - \mu_1^{0} = -\Pi \cdot \overline{V}_1$$

From equ. (26):

$$\Delta\overline{G}_1 = R \cdot T \cdot \left[\ln(1 - \Phi_2) + \left(1 - \frac{1}{x}\right) \cdot \Phi_2 + \varepsilon_1 \cdot \Phi_2^2\right]$$

Polynomial approximation:

$$\ln(1 - \Phi_2) = -\Phi_2 - \frac{\Phi_2^2}{2} - \frac{\Phi_2^3}{3} - \dots$$

$$(\Phi_2 \ll 1)$$

$$\Pi = \left[\Phi_2 + \frac{\Phi_2^2}{2} + \frac{\Phi_2^3}{3} - \Phi_2 + \frac{\Phi_2}{x} - \varepsilon_1 \cdot \Phi_2^2\right] \cdot \frac{R \cdot T}{\overline{V}_1}$$

$$\Pi = \left[\frac{\Phi_2}{x} + \left(\frac{1}{2} - \varepsilon_1 \right) \cdot \Phi_2^2 + \frac{\Phi_2^3}{3} \right] \cdot \frac{R \cdot T}{\overline{V}_1}$$

$$\Phi_2 = c \cdot v_2 \; ; \; x = \frac{\overline{\overline{V}}_2}{\overline{\overline{V}}_1}; \; v_i = \frac{\overline{V}_i}{M_i}$$

c = polymer concentration; v_2 = partial specific volume of the polymer.

$$\Pi = R \cdot T \cdot \left[\frac{cv_2 \overline{V}_1}{\overline{\overline{V}}_1 \overline{\overline{V}}_2} + \left(\frac{1}{2} - \varepsilon_1 \right) \cdot \frac{v_2^2}{\overline{\overline{V}}_1} \cdot c^2 + \frac{1}{3} \cdot \frac{v_2^3}{\overline{\overline{V}}_1} \cdot c^3 \right] (35a)$$

$$\Pi = R \cdot T \cdot \left[\frac{c\overline{V}_2}{M_2 \overline{V}_2} + \frac{\overline{V}_2^2}{M_2^2 \overline{V}_1} \cdot \left(\frac{1}{2} - \varepsilon_1 \right) \cdot c^2 + \frac{1}{3} \cdot \frac{\overline{V}_2^3}{M_2^3 \overline{V}_1} \cdot c^3 \right]$$
(35b)

$$\frac{\Pi}{c} = R \cdot T \cdot \left[\frac{1}{\overline{M}_n} + \frac{\overline{V}_2^2}{M_n^2 \cdot \overline{V}_1} \cdot \left(\frac{1}{2} - \varepsilon_1 \right) \cdot c + \frac{1}{3} \cdot \frac{\overline{V}_2^3}{\overline{M}_n^3 \cdot \overline{V}_1} \cdot c^2 \right]$$
(35c)

$$\boxed{\frac{\Pi}{c} = R \cdot T \cdot \left[\frac{1}{\overline{M}_n} + A_2 \cdot c + A_3 \cdot c^2 + \cdots \right]}$$
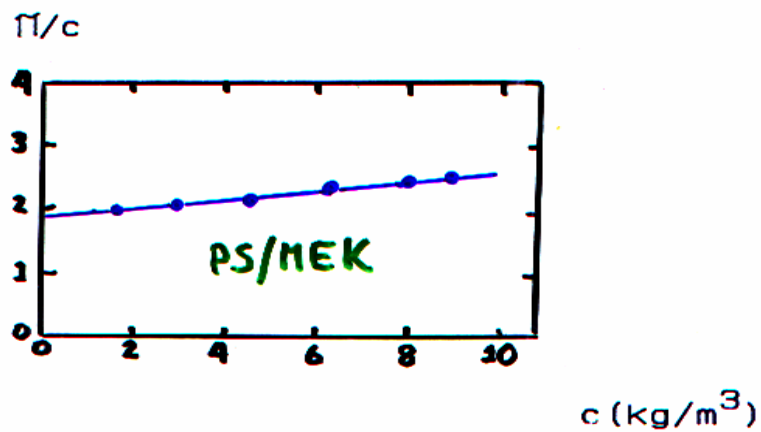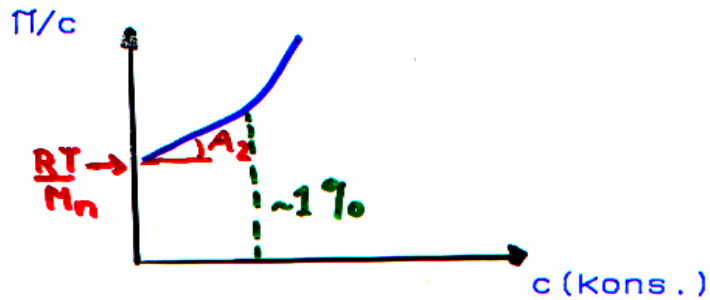
(35d)

Where the *second virial coefficient* is:

$$A_2 = \frac{\overline{V}_2^2}{\overline{M}_n^2 \cdot \overline{V}_1} \cdot \left(\frac{1}{2} - \varepsilon_1\right)$$

At low concentrations (c < 1%)

$$\Pi = \frac{R \cdot T \cdot c}{\overline{M}_n} \qquad \text{(Van't Hoff's equation)}$$

At high concentrations:

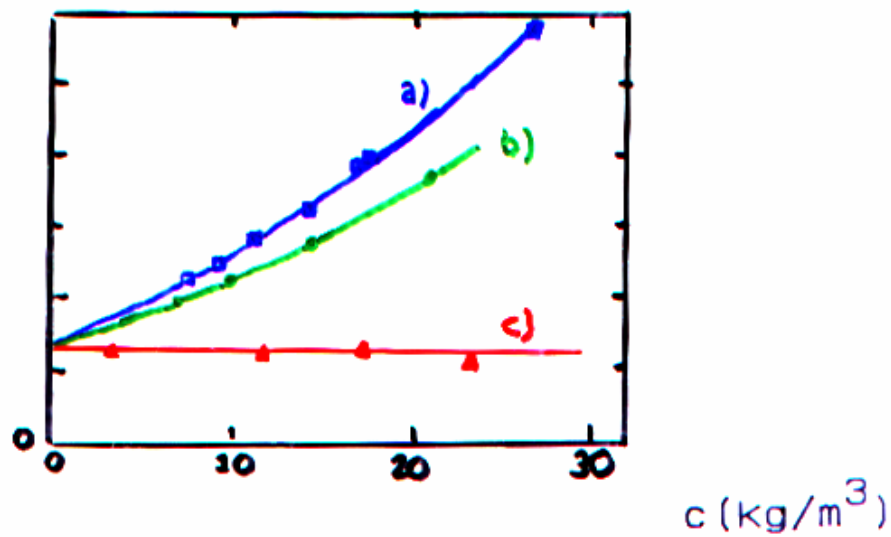$$\frac{\Pi}{c} = R \cdot T \cdot \left(\frac{1}{M_n} + A_2 \cdot c + A_3 \cdot c^2 + \cdots\right)$$
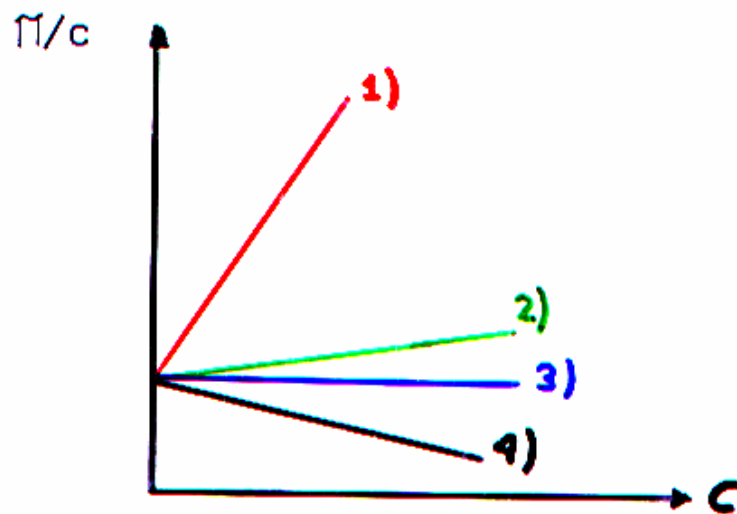
Low concentrations and different thermodynamic

conditions. We examine the following system:

a)   PMMA/toluene

b)   PMMA/Acetone

c) PMMA/Acrylnitrile (θ) $\varepsilon_1 = 0.5$; $A_2 = 0$

1)   Rods and coils in *good solvents*

2)   Compact spheres

3)   Coils in θ-*solvents*

4)   *Poor* solvents $A_2 < 0$

Viscosity

Definition of viscosity:
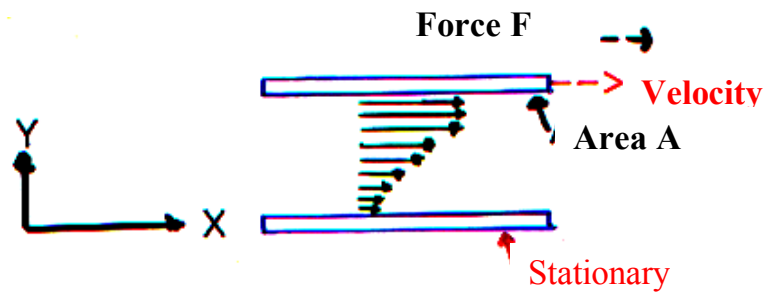
The *viscosity of a liquid* is an expression for its resistance to flow.

Newtonian liquids at *laminar flow*:

$$\frac{F}{A} = \frac{\eta \cdot dv}{dy} \; ; \; \eta = \text{viscosity} \tag{36}$$

The relation between *the force F,* that pulls the plate with an *area A* in contact with the liquid, is called *shear stress* $\sigma = \dfrac{F}{A}$. The relation $\dfrac{dv}{dy}$ is called *shear rate* $\gamma \equiv \dfrac{dv}{dy}$

$$\eta = \frac{\dfrac{F}{A}}{\dfrac{dv}{dy}} = \frac{\sigma}{\gamma} = \frac{\text{shear stress}}{\text{shear rate}} \qquad (37)$$

For *Newtonian liquids,* this *relation is constant. The dimension* for the quantities is:

$$\sigma = \frac{N}{m^2} \; ; \; \gamma = s^{-1} \; ; \; \eta = \frac{N \cdot s}{m^2}$$

Non-Newtonian liquids.
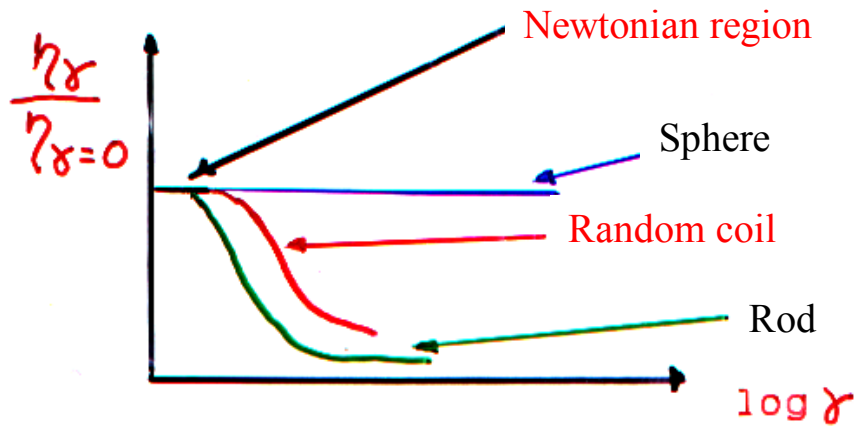
Generally the *broadness of the Newtonian region* will *decrease* with *increasing molecular weight*.

Viscosity in polymer solutions

In a polymer solution, the change in the viscosity is dependent of a number of factors:

- *Solvent* (thermodynamically good or poor solvents)

- *Type of polymer* (size and conformation)

- *The molecular weight of the polymer*

- *The polymer concentration*

- *Temperature*

Einstein's equation:

$$\eta_s = \eta_0(1 + 2.5 \cdot \Phi_2) \qquad (38)$$
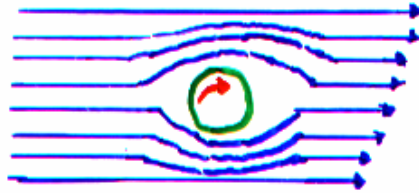
η_s = the solution viscosity
η_0 = the solvent viscosity
Φ_2 = the volume fraction of particles

Equ. (38) is valid for *rigid spheres at low*

concentrations.

For particles of other geometric shapes than spherical,

the following relation is valid:
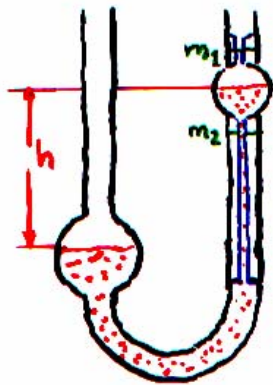
$$\eta_s = \eta_0 \cdot (1 + \beta \cdot \Phi_2) \qquad\qquad (39)$$

where the parameter β is a function of the *asymmetry of the molecule*.

Different types capillary viscosity meters:
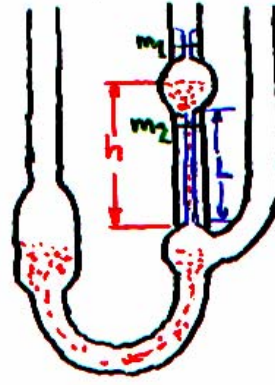
Rotational movement of the polymer molecule
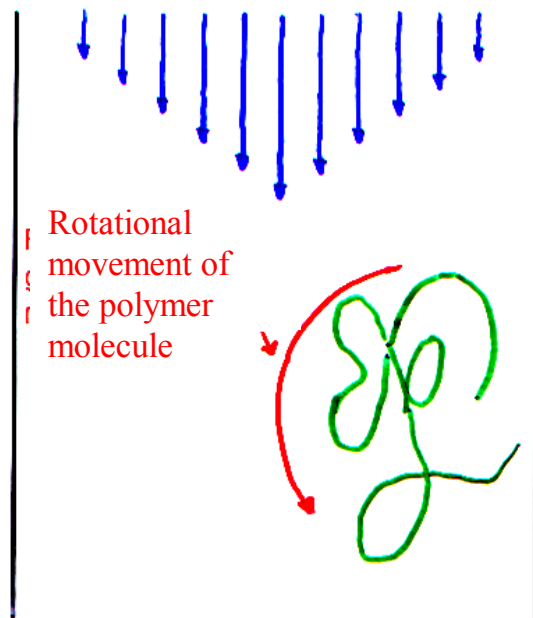
Ostwald: dependent on the volume of the liquid

Ubbelohde: *not* dependent on the volume of the liquid

Ostwald   Ubbelohde

Poiseuilles equation:

$$\frac{dV}{dt} = \frac{\pi r^4 \cdot \bar{p}}{8\eta L}$$ (40)

r   = capillary radius

$\frac{dV}{dt}$ = the volume of a liquid that flows through the

      capillary

L   = the length of the capillary

η   = viscosity

$\bar{p}$ = the average pressure that produces flow

$$\bar{p} = h \cdot \rho \cdot g$$ (41)

h = the level of the liquid

ρ = the density of the liquid

g = the acceleration of gravity

If we substitute equ. (41) in (40) and assumes

constant flow velocity we get:

$$\boxed{\eta = \frac{\pi \cdot r^4 \cdot h \cdot \rho \cdot g \cdot t}{8 \cdot L \cdot V}} \qquad (42)$$

Equ. (42) is valid for *Newtonian flow*.

Reynolds number: $R_{ey} = \dfrac{2 \cdot V \cdot \rho}{\pi r \cdot \eta \cdot t} < 1000$ (Laminar flow)

$R_{et} > 1000$ (turbulent flow)

Determination of the intrinsic viscosity [η]

Relative viscosity:
$$\eta_r = \frac{\eta}{\eta_0} = \frac{t \cdot \rho}{t_0 \cdot \rho_0}$$

0 indicates solvent.

In dilute solutions, $\rho \approx \rho_0$.

Specific viscosity:
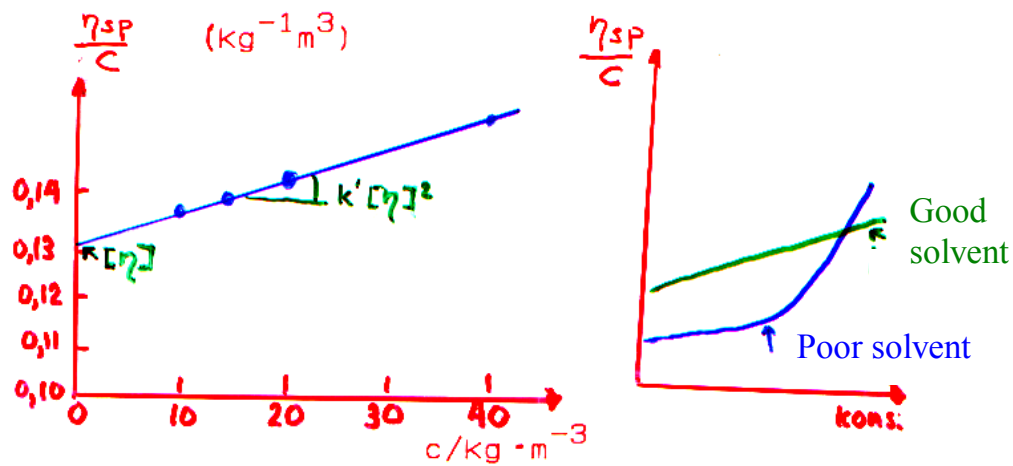$$\eta_{sp} = \eta_r - 1 = \frac{t - t_0}{t_0}$$

Reduced viscosity:
$$\frac{\eta_{sp}}{c}$$

Intrinsic viscosity:
$$[\eta] = \lim \cdot \frac{\eta_{sp}}{c} \; ; \quad c \to 0$$

Empirical relation that represents the concentration dependence of the reduced viscosity:

$$\boxed{\frac{\eta_{sp}}{c} = [\eta] + k' \cdot [\eta]^2 \cdot c} \qquad (43)$$

k′ = Huggins constant.

Flexible polymer coils in dilute solutions:

k′ ≈ 0.5 (θ-conditions); k′ < 0.5 (good conditions)

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Staudinger-Mark-Houwinks equation

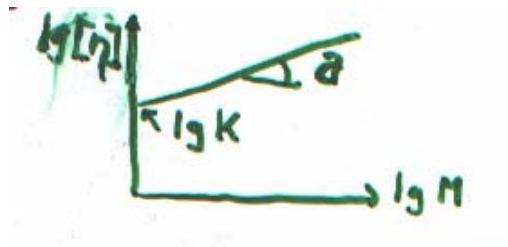Experimental determination of the relation between [η] and M.

$$\boxed{[\eta] = K \cdot M^a} \qquad (44)$$

Relation between molecular shape and exponent

Sphere: $[\eta] = 2.5 \cdot M^0$; $a = 0$

Coil:
$\begin{cases} \textit{Compact}: [\eta] = K \cdot M^{0.5}; a = 0.5 \\ \textit{Random} \text{ (good conditions)}: [\eta] = K \cdot M^{0.7} \\ \textit{Random} \text{ (}\theta\text{-conditions)}: [\eta] = K \cdot M^{0.5} \end{cases}$

Rod: $[\eta] = K \cdot M^{1.8}$; $a = 1.8$

Random coils and Flory-Fox equation

$$\eta_s = \eta_0(1 + 2.5 \cdot \Phi_2)$$

η_s = solution viscosity
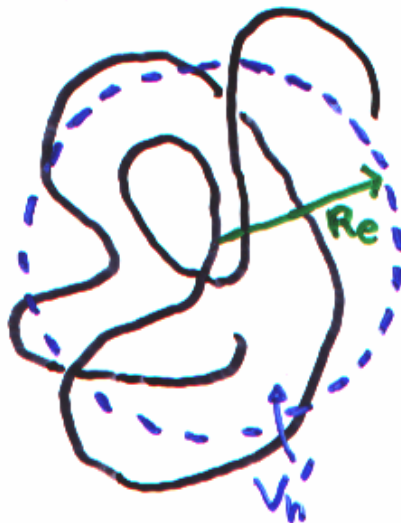
$\Phi_2 = c \cdot v_h$; v_h = hydrodynamic volume

$$\eta_r = \frac{\eta_s}{\eta_0} = 1 + 2.5 \cdot c \cdot v_h$$

$$\eta_{sp} = \eta_r - 1 = 2.5 \cdot c \cdot v_h$$

$$\lim_{c \to 0} \frac{\eta_{sp}}{c} = [\eta] = 2.5 \cdot v_h \qquad (45)$$

Let us assume that a *random coil* will behave as an

equivalent sphere with a radius R_e:

$$R_e = \psi \cdot R_G; \; \psi \approx 0.8$$

The *hydrodynamic volume* for the particle is:

$$v_h' = \frac{4\pi \cdot \psi^3 \cdot R_G^3}{3}$$

This is the hydrodynamic volume pr. sphere, but we

are interested in *the hydrodynamic volume pr. weight*

unit of the macromolecule.

$$v_h = \frac{v_h' \cdot N_A}{M}$$

$$v_h = \frac{4\pi \cdot \psi^3 \cdot R_G^3 \cdot N_A}{3 \cdot M}$$

From Einstein's equation (45) we get:

$$[\eta] = \frac{\phi \cdot R_G^3}{M} \qquad\qquad (46)$$

$\phi \approx 2.8 \cdot 10^{21}$ (θ-solvent); $\phi \approx 2.0 \cdot 10^{21}$ (in good

solvents). Equ. (46) *(Flory-Fox equation)*

Kirkwood-Riseman:

$$[\eta] = \frac{N_A \cdot f_0 \cdot b \cdot R_G^2}{6\pi \cdot \eta_0 \cdot M} \quad ; \quad [\eta] \propto \frac{R_G^2 \cdot R_D}{M} \quad (47)$$
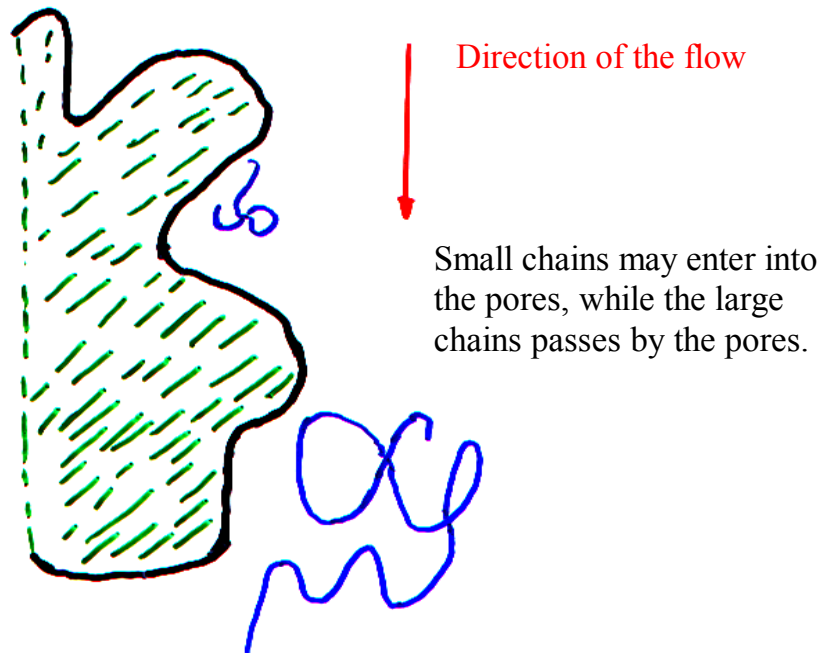
$f_0 = (6\pi\eta_0 R_D)$ the friction coefficient when $c \to 0$

η_0 = solvent viscosity

b = bond length

R_D = hydrodynamic or dynamic radius

Gel permeatation chromatography (GPC)

Direction of the flow

Small chains may enter into the pores, while the large chains passes by the pores.

GPC is a method for *separation* of large molecules (separates by molecular size). This method is used to determine the *molecular weight* and the *molecular weight distribution* $\left(\dfrac{\overline{M}_w}{\overline{M}_n}\right)$ of polymers.

Principal sketch of GPC equipment
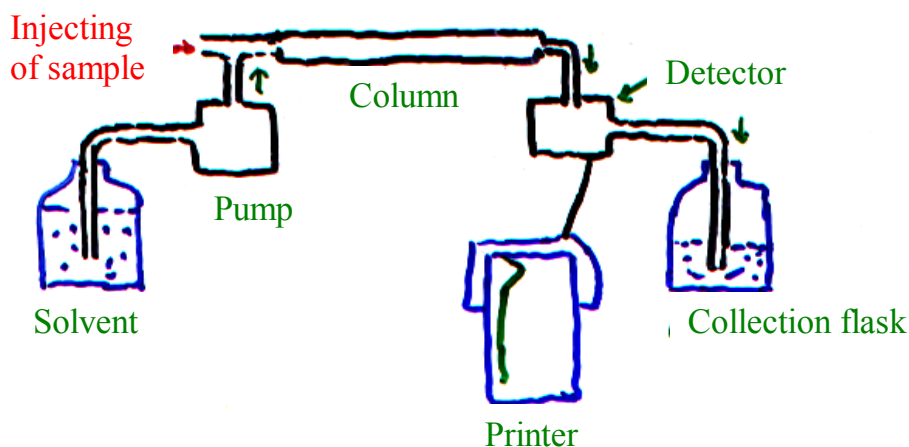
GPC is a method where the *polymers are fractionated according to the size* of the molecules, and accordingly by the *molecular weight*. However, the *molecular weigh* may not *be determined directly*, but only by *calibrating of the system* by measuring the *eludating volume* for a *number of monodisperse polymer fractions* with a known molecular weight.

<u>Illustration of a GPC experiment</u>.
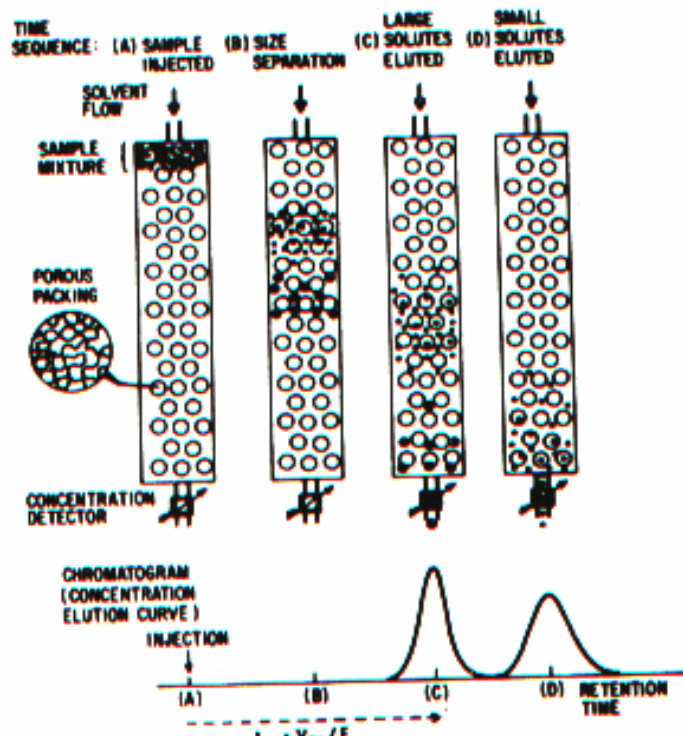
The gel particles consist of a *cross-linked polymer*

and have *variable pore sizes*.

Polymer: Ex.: Styragel (co-polymerization of styrene

with divinyle benzene) and dextran

(sephadex)

Pore diameter: 25-10.000 Å.

The stationary phase of the column: The gel particles included the liquid that is bond inside the pores.

The mobile phase of the column: The eludating sample that flows through the column between the gel particles.

The sample with polymer: A small volume is injected at the top of the column.

Detector: UV-absorption, refractive index (differential refractometer).

Retention time: The time that a certain fraction is in the column.

The flow of the polymer particles through the column

is a function of the *Brownian motion and the size of*

the polymer molecules.

Calibrating: With monodisperse polymers (PS, PEO)

of a known molecular weight.

$$\log M = a + b \cdot V_r$$

M = molecular weight
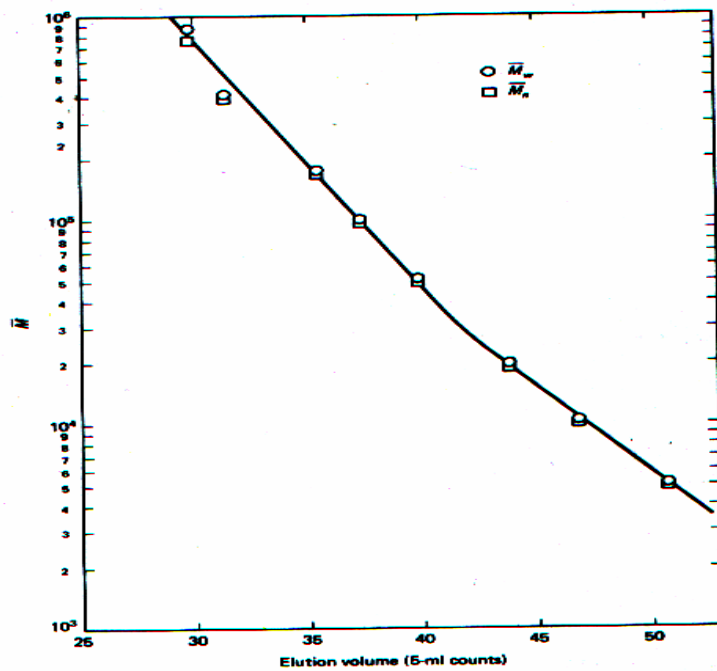V_r = retention volume
a and b are constants

Fig. 15.9   Molecular weight of monodisperse polystyrene standards as a function of elution volume in tetrahydrofuran. [From M. Kolinsky and J. Janca, *J. Polymer Sci., Chem. Ed.*, 12, 1181 (1974).]

Universal calibrating: [η]·M plotted against V$_r$·[η]·M

correspond to a hydrodynamic volume

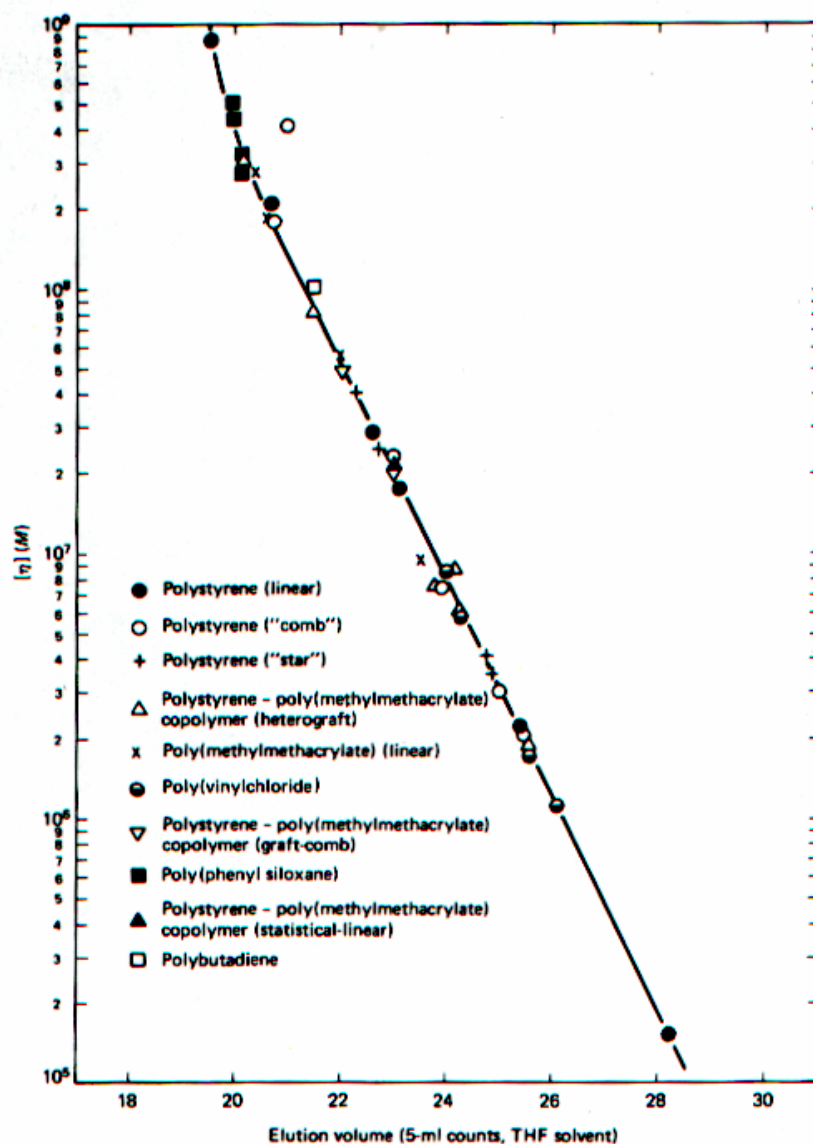$$\left([\eta] = \frac{\psi \cdot R_G^3}{M} \right)$$

Fig. 15.8 Universal calibration in gel-permeation chromatography for a variety of polymers in tetrahydrofuran. [Reproduced from Z. Grubisic, P. Rempp and H. Benoit, *Polymer Lett.*, **5**, 753 (1967); with permission of John Wiley & Sons, Inc., New York.]

Light scattering

Inhomogeneities in the sample (fluctuations in refractive index) causes light scattering:

a)   Density fluctuations

b)   Concentration fluctuations

Light scattering (static) gives information of *molecular weight* (M_w), *the radius of gyration* (R_G) and *thermo dynamical properties* (e.g. A_2).

Principal sketch of light scattering equipment

Sample cell

Inncomming light beam

I_0, λ

Detector
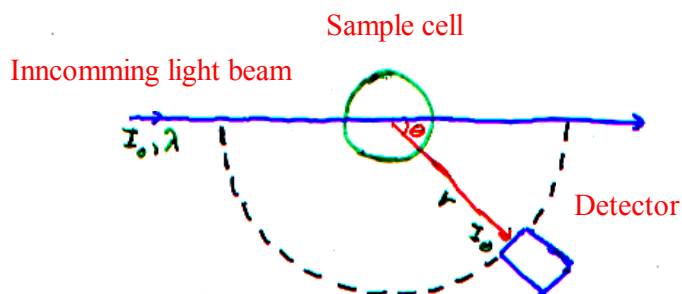
<u>Scatter of light polarized in a plane from one particle</u>:
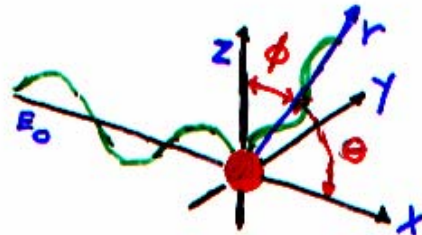
Let us consider the scatter from light polarized in a plane, with a frequency ν, and wavelength λ, from one particle. The electric field, E, may be written in the following way:

$$E = E_0 \cdot \cos(2\pi\nu t)$$

E_0 = max. amplitude,
ν = frequency
λ = wave length
t = time

An *oscillating field* will cause the introduction of an *oscillating dipole moment*, μ, in the molecule:

$$\mu = \gamma \cdot E = \gamma \cdot E_0 \cdot \cos(2\pi\nu t); \gamma = \text{polarize ability.}$$

For *polarized light* of a wavelength λ, Rayleigh discovered the following relation between the intensity I_O of the incoming light and the intensity I_S of the scattered light from *one particle*, at an angle φ with respect to the incoming light:

$$\boxed{\frac{I_s{'}}{I_0{'}} = \frac{16\pi^4\gamma^2}{r^2\lambda^4} \cdot \sin^2 \phi} \qquad (48a)$$

r = distance from the particle to the point of observation

φ = the angle between the axis of polarization and the direction of the scattered light.
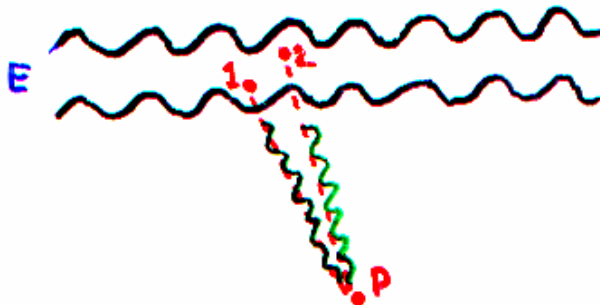
For *unpolarized light* the analogue expression is:

$$\boxed{\frac{I_s'}{I_0'} = \frac{8\pi^4\gamma^2}{r^2\lambda^4} \cdot (1 + \cos^2\theta)}$$

(48b)

θ = the angle between the incoming and the scattered light.

We got $I_s \propto \lambda^{-4}$ which means that blue light ($\lambda \approx 450$ nm) (blue sky) scatter considerably more than red light ($\lambda \approx 630$ nm) (red sunset).

Constructive and destructive interference

$$\psi_1 = A \cdot \cos(2\pi \cdot \nu \cdot t + \delta_1) \, ; \, A = \text{ amplitude}$$

$$\psi_2 = A \cdot \cos(2\pi \cdot v \cdot t + \delta_2)$$

δ_1 and δ_2 represents the phase shift from particle 1 and 2, respectively. (The particles have unequal distance from the source of radiation and additionally the distance between the particles and the detector is unequal.)

The collected succession of waves at P is:

$$\psi = \psi_1 + \psi_2$$

$$\psi = A \cdot \cos(2\pi \cdot v \cdot t + \delta_1) + A \cdot \cos(2\pi \cdot v \cdot t + \delta_2)$$

$\Delta\delta = \delta_2 - \delta_1 = n_1 \cdot 180°$; n_1 is an odd number multiple of 180°, the succession of waves cancels each other out (destructive interference).

$\Delta\delta = 0$, or a multiple of 360°, the succession of waves will amplify each other (constructive interference).

If the two particles move independent of each other (ideal gas), *all Δδ will be equal probable* → the effect of the interference will at average *equal 0*.

At the observation point:

$$I_s = I_{s,1} + I_{s,2}$$

Solutions of macromolecules

Rayleigh scattering:

$$R_G < \frac{\lambda}{20}$$

We will now regard the *excess light scattering* that are due to *particles* dissolved in the liquid.

Fluctuation theory (Einstein): One imagines that the liquid is divided into *volume elements* that are *less than the wavelength of the light*.

The volume elements have a *fluctuating concentration* of macromolecules. These *concentration fluctuations* must necessarily be *dependent* of the *size of the macromolecules* $\left(\overline{M}_W, R_G\right)$ and *interactions* in the system (A_2: thermodynamic properties).

Ideal solution: Classical electro magnetic theory:

$$\boxed{n^2 - n_0^2 = 4\pi \cdot N \cdot \gamma} \qquad (49)$$

$N = \dfrac{\text{number} \quad \text{of} \quad \text{particles}}{\text{volume unit}}$; n_0 and n is the refractive index of solvent and solution, respectively.

$$(n - n_0) \cdot (n + n_0) = 4\pi \cdot N \cdot \gamma$$

$$\gamma = \underbrace{\frac{n + n_0}{4\pi}}_{(1)} \cdot \underbrace{\frac{n - n_0}{c}}_{(2)} \cdot \underbrace{\frac{c}{N}}_{(3)}$$

(1) In a dilute solution: $n + n_0 \approx 2n_0$

(2) $\dfrac{dn}{dc}$ refractive index increment

(3) $\boxed{N = c \cdot \dfrac{N_A}{M}}$ (50)

$$\boxed{\gamma = n_0 \cdot \frac{dn}{dc} \cdot \frac{M}{2\pi \cdot N_A}} \qquad (51)$$

We put this into Rayleigh's equ. (48b):

$$\boxed{\begin{aligned}
\frac{I'_s}{I_0} &= 8\pi^4 n_0^2 \cdot \left(\frac{dn}{dc}\right)^2 \cdot M^2 \cdot \frac{1 + \cos^2\theta}{r^2 \lambda^4 (2\pi)^2 N_A^2} = \\[2mm]
&= 2\pi^2 \cdot n_0^2 \cdot \left(\frac{dn}{dc}\right)^2 \cdot M^2 \cdot \frac{1 + \cos^2\theta}{\lambda^4 r^2 N_A^2}
\end{aligned}} \qquad (52)$$

I_s' is the scatter from one particle, but we want to know the scatter from N particles ($N = c \cdot \dfrac{N_A}{M}$):

$$\boxed{\frac{I_s}{I_0} = 2\pi^2 \cdot n_0^2 \cdot \left(\frac{dn}{dc}\right)^2 \cdot \frac{\left(1 + \cos^2\theta\right) \cdot c \cdot M}{\lambda^4 \cdot r^2 \cdot N_A}} \qquad (53)$$

$$\frac{I_s}{I_0} \cdot \frac{r^2}{1 + \cos^2\theta} = R_\theta = 2\pi^2 \cdot n_0^2 \cdot \left(\frac{dn}{dc}\right)^2 \cdot \frac{1}{\lambda^4 N_A} \cdot c \cdot M$$

R_θ = reduced scattered intensity

$$R_\theta = R_\theta^{\text{solution}} - R_\theta^{\text{solvent}}$$

$$K = 2\pi^2 \cdot n_0^2 \cdot \left(\frac{dn}{dc}\right)^2 \cdot \frac{1}{\lambda^4 N_A}$$

K = constant for a given polymer system

$$R_\theta = K \cdot c \cdot M$$

$$\boxed{\frac{K \cdot c}{R_\theta} = \frac{1}{M}} \tag{54}$$

Compare the expression $\dfrac{\Pi}{R \cdot T \cdot c} = \dfrac{1}{M}$ for osmotic pressure at ideal conditions.

Real solution (at normal concentrations)

The concentration fluctuations are also dependent the thermo dynamical conditions in the solution.

Thermo dynamics may be described by the *osmotic*

compressibility, $\dfrac{d\Pi}{dc}$

The degree of *destructive interference will increase*

with $\dfrac{d\Pi}{dc}$ and the light scattering will be *reversible*

proportional to $\dfrac{d\Pi}{dc}$.

Debye: $\boxed{R_\theta = \dfrac{K \cdot R \cdot T \cdot c}{\dfrac{d\Pi}{dc}}}$ (55)

$$\frac{\Pi}{c} = R \cdot T \cdot \left(\frac{1}{M} + A_2 c + A_3 c^2 + \cdots \right)$$

$$\frac{d\Pi}{dc} = R \cdot T \cdot \left(\frac{1}{M} + 2A_2 c + 3A_3 c^2 + \cdots \right)$$

$$R_\theta = \frac{K \cdot R \cdot T \cdot c}{R \cdot T \cdot \left(\dfrac{1}{M} + 2A_2 c + 3A_3 c^2 + \cdots \right)}$$

$$\boxed{\frac{K \cdot c}{R_\theta} = \frac{1}{M} + 2A_2 c + 3A_3 c^2 + \cdots} \qquad (56)$$
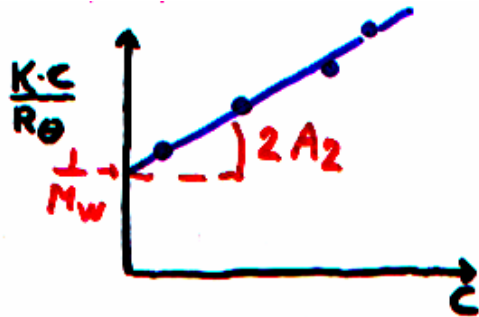
Rayleigh-Gans scattering $(\frac{\lambda}{20} < R_G < \frac{\lambda}{2})$

In the preceding discussion, we have considered particle where $R_G < \dfrac{\lambda}{20}$. When the dimensions of the *scattering particle are larger than this*, the phase difference becomes large enough to give *destructive interference*. Large particles give destructive interference that has *the greatest effect at large angles*.
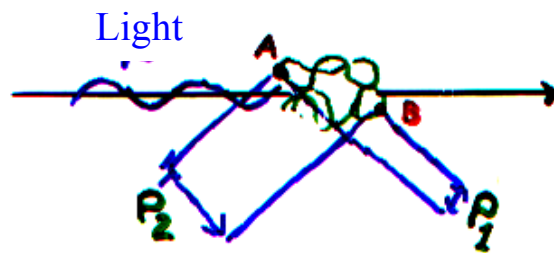
At *zero angle* we will *not get any phase shift*, and thereby *no destructive interference*.
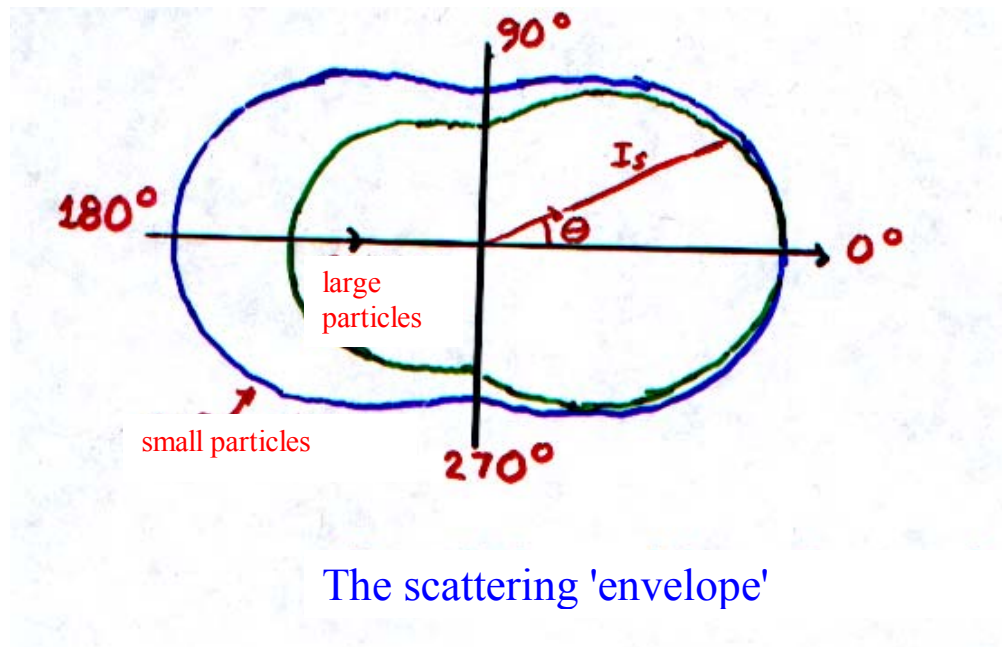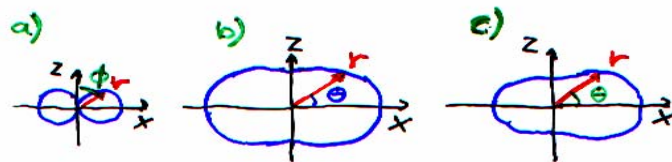
Illustration of scatter from large and small particles.

The scattering 'envelope'

Illustration of the scattering envelope in the x-z plane

at different conditions:

a) *Rayleigh-scattering* $(R_\theta < \dfrac{\lambda}{20})$ of *light polarized in*

  a plane

b) *Rayleigh-scattering* $(R_\theta < \dfrac{\lambda}{20})$ *of unpolarized light*

c) *Rayleigh-Gans-scattering* $\quad(\dfrac{\lambda}{20} < R_\theta < \dfrac{\lambda}{2})\quad$ of

  unpolarized light

The distribution of the angle of the scattered light is

dependent of several different factors:

a) the size of the particle

b) the shape of the particle

c) interactions between the particles

d) the size distribution of the particles

At *low scattering angles*, θ, and at *low concentrations*, the *angular dependency is independent of the shape of the particle* and only dependent on the *average radius of gyration* of the particle.

In practical treatment of light scattering data, we define a function P(θ) = *the particle-scattering factor or the form factor.*

1/P(θ)

Spheres

Random coils

Rods

$Sin^2(θ/2)$
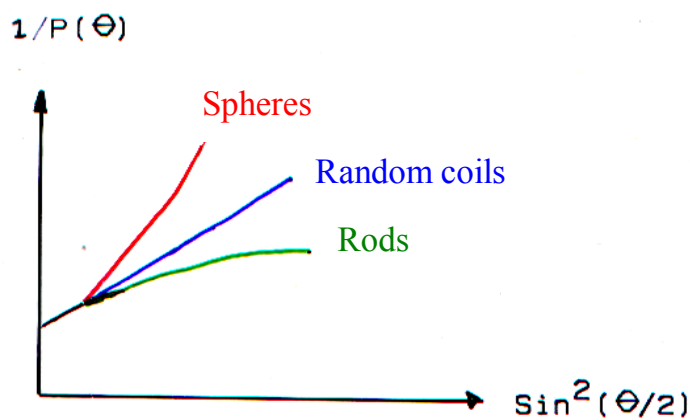
$$P(\theta) = \frac{R(\theta)\,(\text{real particle})}{R(\theta)(\text{the same particle if it had produced Rayleigh - scattering})}$$

$$P(\theta) \to 1 \text{ when } \theta \to 0 \text{ and } P(\theta) < 1 \text{ for } \theta > 0$$

$$(R_\theta)_{real} = P(\theta) \cdot (R_\theta)_{Rayleigh}$$

From equ. (56)

$$\boxed{\frac{K \cdot c}{R_\theta} = \frac{1}{P_\theta} \cdot \left(\frac{1}{M} + 2A_2 \cdot c + 3A_3 \cdot c^2 + \cdots \right)} \qquad (57)$$

$$\boxed{\underset{\theta \to 0}{\text{Lim}}\left(\frac{1}{P(\theta)} \right) = 1 + \frac{16\pi^2 \cdot R_G^2 \cdot \sin^2 \cdot \left(\frac{\theta}{2} \right)}{3 \cdot \lambda^2}} \qquad (58)$$

We may now write the light scattering equation (57)

in this way

$$\boxed{\frac{K \cdot c}{R_\theta} = \left(1 + \frac{16\pi^2 \cdot R_G^2 \cdot \sin^2 \cdot \left(\frac{\theta}{2} \right)}{3 \cdot \lambda^2} \right) \cdot \left(\frac{1}{M} + 2A_2 \cdot c \right)} \; (59)$$

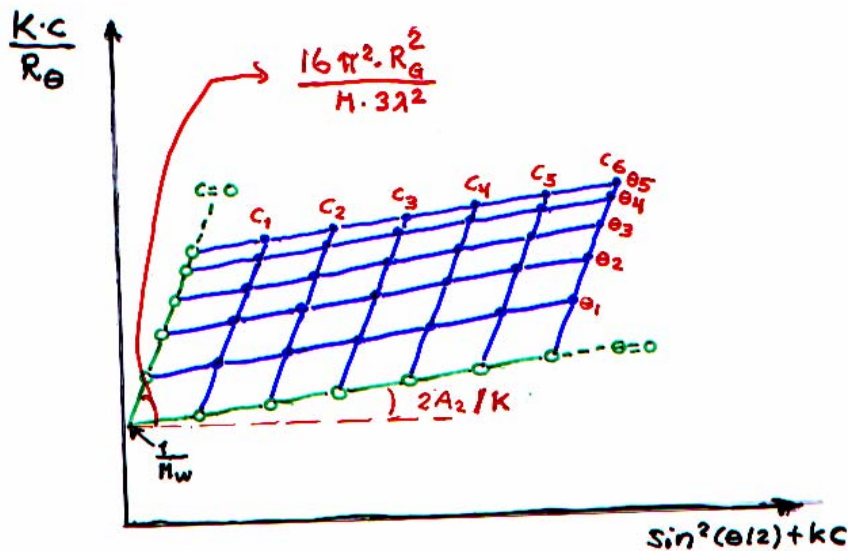In order to determine the molecular weight, we have to extrapolate to both $c = 0$ and $\theta = 0$.

$$c \rightarrow 0; \quad \frac{K \cdot c}{R_\theta} = \frac{1}{M} \cdot \left(1 + \frac{16\pi^2 \cdot R_G^2 \cdot \sin^2\left(\frac{\theta}{2}\right)}{3\lambda^2} \right)$$

$$\theta \rightarrow 0; \quad \frac{K \cdot c}{R_\theta} = \frac{1}{M} + \frac{2A_2 \cdot c}{k}$$

In a *Zimm-diagram* $\dfrac{K \cdot c}{R_\theta}$ is plotted against $\sin^2 \cdot \left(\dfrac{\theta}{2}\right) + k \cdot c$, where k is a constant (2000) that is used to scatter the measured data.

RESULTS

Polymer		$\overline{R}_G(\text{Å})$
Serum albumin $(M = 6.6 \cdot 10^4)$ (spherical)		29.8
Myosin $(M = 4.9 \cdot 10^5)$	(rod)	468
Polystyrene $(M = 1 \cdot 10^5)$	(coil)	100
DNA $(M = 4 \cdot 10^6)$	(rod)	1170

Polystyrene/butanone

$\overline{M}_W \cdot 10^{-3}$	$\overline{R}_G(\text{Å})$
1770	437
940	306
524	222
230	163

DIFFUSION

The force for diffusion is the gradient of the chemic potential $\left(\dfrac{\partial \mu}{\partial x}\right)$. Substances diffuse spontaneously from a region with a high chemical potential to a region with a low chemical potential; that is from a concentrated to a dilute solution.
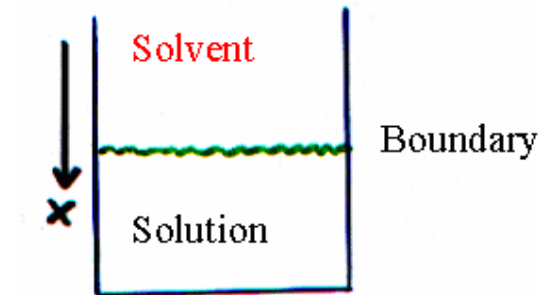
When we have a *concentration gradient* in a solution, we get a *flux* of matter, in a way that leads to a *leveling out* of the *concentration gradient*.

$$\boxed{J = -D \cdot \frac{\partial c}{\partial x}}$$ (Fick's law) (60)

$$J = \text{flux} \left(kg \cdot m^{-2} \cdot s^{-1} \right)$$

$$D = \text{the diffusion coefficient } (m^2 \cdot s^{-1})$$

$$c = \text{cons.} \left(\frac{kg}{m^3} \right)$$

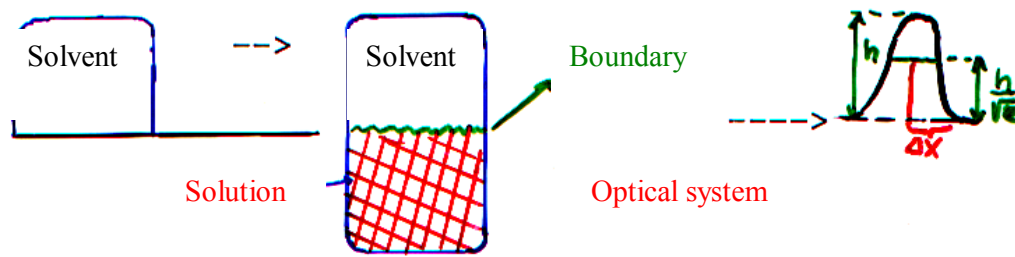In order to eliminate the flux, we may use the *continuity equation*:

$$\boxed{\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x}}$$ (61)
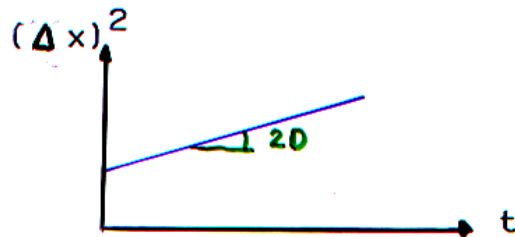
Combination of (60) and (61) give:

$$\boxed{\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}}$$ (Fick's second law) (62)

--

Classical gradient technique

Solvent   -->   Solvent   Boundary

Solution   Optical system

$$(\Delta x)^2 = 2D \cdot t \qquad \text{(Brownian motion)}$$

$(\Delta x)^2$

$$\angle 2D$$

t

The flux of a substance is related to the *negative*

gradient of the *chemical potential* $\left(-\dfrac{\partial \mu}{\partial x}\right)$:

$$\boxed{J = -L \cdot \frac{\partial \mu}{\partial x}} \qquad\qquad (63)$$

L = phenomenological coefficient

Ideal solutions:

$$\mu = \mu^0 + R \cdot T \cdot \ln c$$

$$\frac{\partial \mu}{\partial x} = \frac{\partial \mu}{\partial c} \cdot \frac{\partial c}{\partial x} = \frac{R \cdot T}{c} \cdot \frac{\partial c}{\partial x}$$

Combination with equ. (63) gives:

$$\boxed{J = -\frac{L \cdot R \cdot T}{c} \cdot \frac{\partial c}{\partial x}} \qquad\qquad (64)$$

The flux may also be expressed in another way:

$$J = c \cdot v = -L \cdot \frac{\partial \mu}{\partial x}$$

v = velocity

c = concentration

In diffusion, the *force* (pr. mol) $-\frac{\partial \mu}{\partial x}$ *is balanced by*

the frictional force

$$F_{fr} \, (\text{pr. molecule}) = f_0 \cdot v$$

$$F_{fr} \, (\text{pr. mol}) = f_0 \cdot v \cdot N_A$$

$$f_0 = \text{the frictional coefficient}$$

$$\boxed{c \cdot v = L \cdot f_0 \cdot v \cdot N_A \rightarrow L = \frac{c}{f_0 \cdot N_A}} \qquad (65)$$

We may now write equ. (64) in this way:

$$\boxed{J = -\frac{c \cdot R \cdot T}{f_0 \cdot N_A \cdot c} \cdot \frac{\partial c}{\partial x} = -\frac{R \cdot T}{f_0 \cdot N_A} \cdot \frac{\partial c}{\partial x}} \qquad (66)$$

Compare equ. (60) with equ. (66):

$$\boxed{c \rightarrow 0 \qquad D_0 = \frac{R \cdot T}{f_0 \cdot N_A}} \qquad (67)$$

when $c \gg 0$

$$D = M \cdot (1 - v_2 \cdot c) \cdot \frac{\dfrac{\partial \pi}{\partial c}}{f \cdot N_A} \qquad (68)$$

$$D = \frac{R \cdot T}{N_A \cdot f} \cdot (1 - v_2 \cdot c) \cdot \left(1 + 2A_2 \cdot M \cdot c + 3A_3 \cdot M \cdot c^2 + \cdot\right) \quad (69)$$
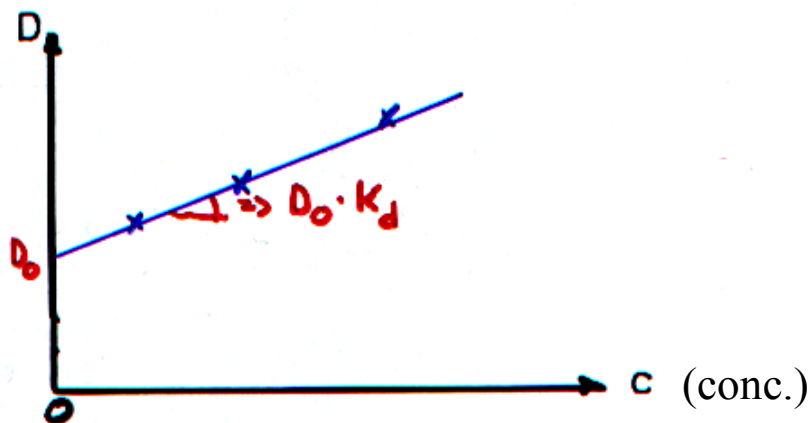
$$D = \left(\frac{R \cdot T}{N_A \cdot f} \right)_{\text{Hydrodynamic factor}} \cdot Q(c)_{\textbf{Thermodynamic factor}}$$

(69a)

The concentration dependence of the diffusion coefficient

$$\boxed{D = D_0(1 + k_d \cdot c)} \; ; \; \text{(empirical equ.)} \qquad (70)$$

k_d = coefficient that is dependent on *hydrodynamic* and *thermodynamic* conditions
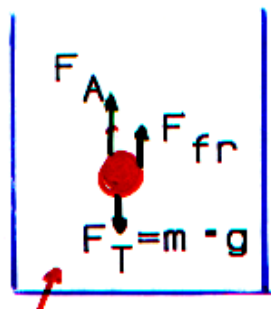

$$k_d = 2A_2M - k_s - v_2$$

ULTRA CENTRIFUGATION (Svedberg)

Velocity centrifugation (50.000-60.000 r.p.m.) gives

hydrodynamic information

Equilibrium centrifugation (5.000-6.000 r.p.m.) gives

thermodynamic information

Velocity centrifugation

Let us first look at a spherical particle (e.g. a ball) that

falls in a liquid medium under the influence of the

gravity force, g:

| m = the mass of the particle |
| v$_2$ = the specific volume of the particle |
| ρ = the density of the liquid |
| g = the gravity acceleration |

Liquid

$$F_T - F_A - F_{fr} = m \cdot a \text{ ; after a short time, } a \approx 0$$

$$F_T = F_A + F_{fr}$$

$$m \cdot g = m \cdot v_2 \cdot \rho \cdot g + F_{fr}$$

m·v₂ represents the volume of displaced liquid

$F_{fr} = m \cdot g(1 - v_2 \cdot \rho)$ represents the upwards pressure

$$m = \frac{M}{N_A} \text{ ; } F_{fr} = f \cdot v$$

f = the friction coefficient, that is dependent of *the size and shape of the particles*, and *the viscosity of the liquid*.

$$\boxed{f \cdot v = \frac{M}{N_A} \cdot (1 - v_2 \rho) \cdot g} \qquad (71)$$

Macromolecules are far too small particles to sediment in the earth's gravitational field, one therefore need to *apply a centrifugal field* (ultra centrifuge) in order to get the molecules to sediment.

Ω = Angular velocity

Solution

F_s = Sentrifug. force
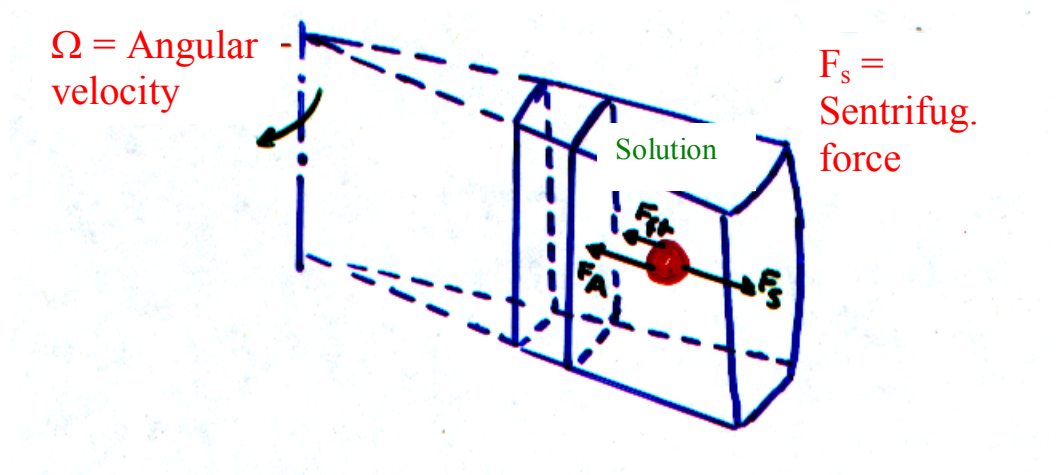
In a *centrifugal field, g is replaced* by $\Omega^2 \cdot r$ (200.000 g), where Ω *is the angular velocity* and *r is the distance from the rotor axis*. Equ. (71) may now be written as:

$$f \cdot v = \frac{M}{N_A} \cdot \left(1 - v_2 \cdot \rho\right) \cdot \Omega^2 \cdot r \qquad (72)$$

Ex.

60 000 r.p.m. $\Omega^2 \cdot r = (2\pi \cdot 1000)^2 \cdot (6\ cm) = 2.38 \cdot 10^6\ cm \cdot s^{-2}$
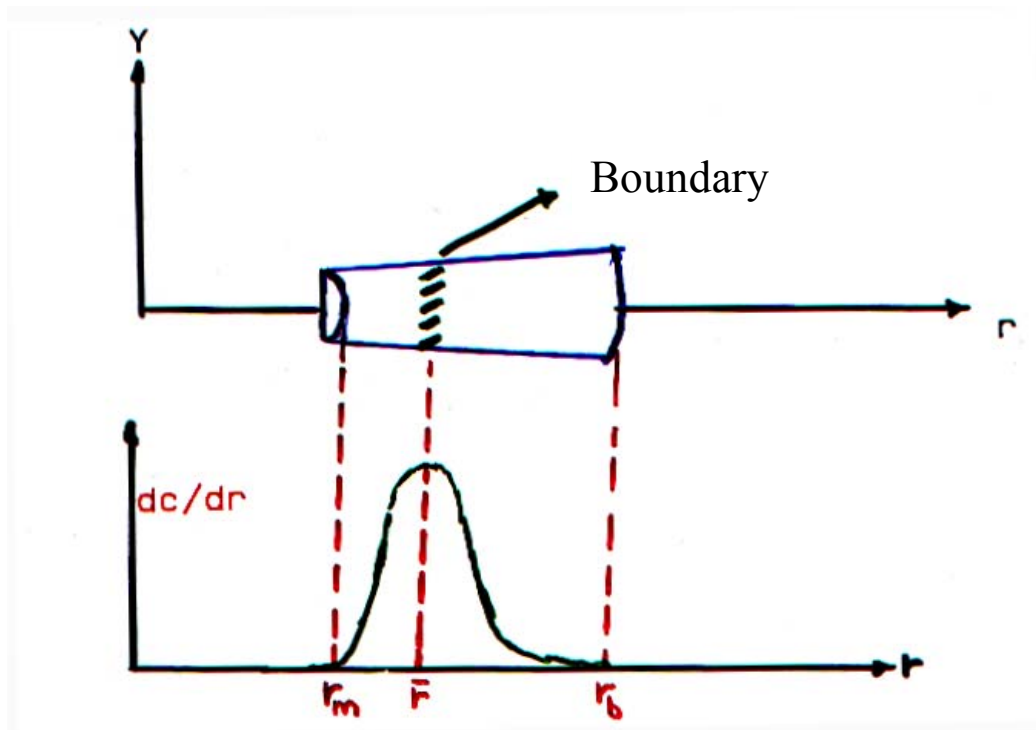
Svedberg introduced a parameter that is called the *sedimentation coefficient*, S:

$$S = \frac{v}{\Omega^2 \cdot r}\ ;\ (v = \frac{dr}{dt}) \qquad (73)$$

A combination of equ. (72) and (73), and when we additionally look at the situation when $c \to 0$:

$$S_0 = \frac{M \cdot (1 - v_2 \cdot \rho_0)}{N_A \cdot f_0} \qquad (74)$$

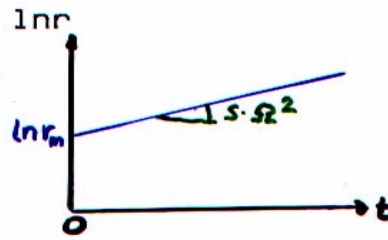111

<u>Illustration of how the boundary may be registered.</u>

The rotor is spinning around the axis with an angular velocity Ω. *Schlieren optics is used to register the concentration gradient*; r_m = the position of the meniscus; $\bar{r}$ = the position of the boundary.

$$S = \frac{\dfrac{dr}{dt}}{\Omega^2 \cdot r}$$

$$\int_{r_m}^{\bar{r}} \frac{dr}{r} = S \cdot \Omega^2 \int_0^t dt$$

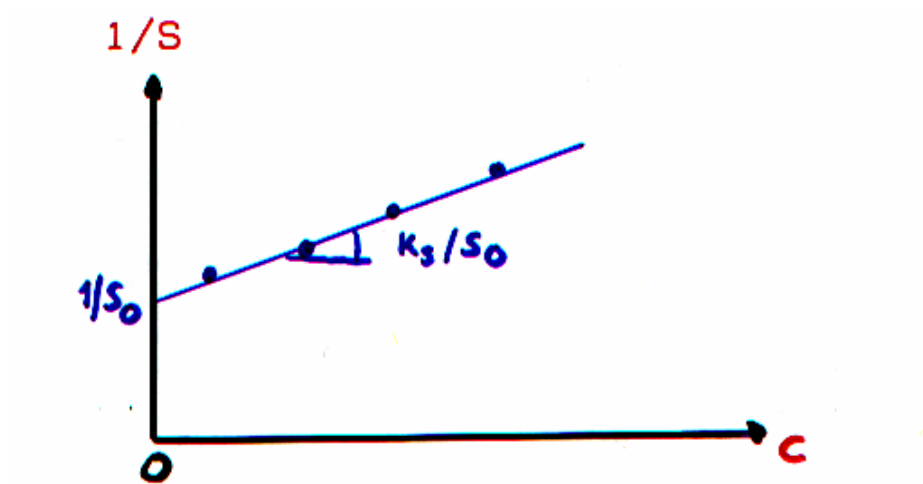$$\ln \cdot \frac{\bar{r}}{r_m} = S \cdot \Omega^2 \cdot t$$

$$\ln \bar{r} = \ln r_m + S \cdot \Omega^2 \cdot t \qquad\qquad (75)$$

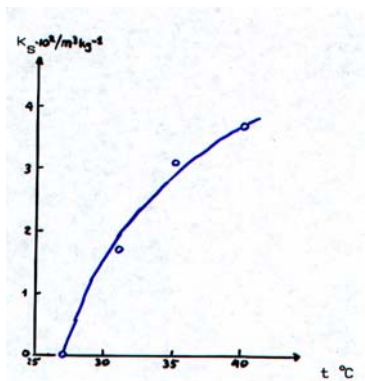## The concentration dependence of the sedimentation coefficient

For random coils, S is dependent on the concentration, and this may be expressed using the following empirical equation:

$$\frac{1}{S} = \frac{1}{S_0} \cdot (1 + k_s \cdot c) \qquad\qquad (76)$$

k_s is a coefficient that expresses the *concentration dependence*. k_s is related to the *hydrodynamic* and *thermodynamic* conditions of the system.

$$k_S = 1.2 \cdot A_2 M + \frac{N_A V_h}{M}$$

$k_s = 0$ at UCST; system: PS(M=390 000)/ cyclohexane (θ=35 ^{o}C)

In order to determine the *molecular weight* in equ..

(74), we need to know f_0. One may determine f_0. from

diffusion measurements (equ. (67)). $D_0 = \dfrac{R \cdot T}{N_A \cdot f_0}$.

By combining equ. (67) and (74), we get the *Svedberg*

equation:

$$\boxed{M = \frac{S_0 \cdot R \cdot T}{D_0 (1 - v_2 \cdot \rho_0)}} \qquad (77)$$

Equilibrium centrifugation

If we let the rotor rotate at a *relatively slow speed*

(5.000-6.000 r.p.m.) we may get *equilibrium in the*

cell, so *no net sedimentation* is taking place. This

usually takes a long time (several days).

$$v \equiv \frac{dr}{dt} = S \cdot \Omega^2 \cdot r \qquad\qquad \text{(see equ. (73))}$$

and the flux is:

$$J_s = c \cdot v = c \cdot S \cdot \Omega^2 \cdot r$$

$$J_D = -D \cdot \frac{dc}{dr} \quad \text{(Fick's 1. law)}$$

At equilibrium:

$$J_s + J_D = 0.$$

Vi assumes an *ideal solution*: $S \cdot \Omega^2 \cdot r \cdot c - D \cdot \dfrac{dc}{dr} = 0.$

$$\frac{S}{D} \cdot \Omega^2 \int_{r_m}^{\bar{r}} r \cdot dr = \int_{c_m}^{\bar{c}} \frac{dc}{c} \;\; ; \; m = \text{meniscus}$$

$$\frac{S \cdot \Omega^2}{2D} \cdot \left(\bar{r}^2 - r_m^2 \right) = \ln \cdot \frac{\bar{c}}{c_m}$$

From equ. (77): $\dfrac{S}{D} = \dfrac{M \cdot (1 - v_2 \cdot \rho)}{R \cdot T}$

$$\frac{M}{2 \cdot R \cdot T} \cdot (1 - v_2 \cdot \rho) \cdot \Omega^2 \cdot \left(\bar{r}^2 - r_m^2\right) = \ln \cdot \frac{\bar{c}}{c_m}$$

$$\boxed{M = \frac{2 \cdot R \cdot T \cdot \ln \dfrac{\bar{c}}{c_m}}{\Omega^2 \cdot (1 - \rho \cdot v_2) \cdot (\bar{r}^2 - r_m^2)}} \qquad (78)$$

Information from equilibrium sedimentation:

- We may *determine the molecular weight* by observing the concentration as a function of the distance (r). The concentration may be measured with the aid of a refractive index detector or UV detection.

- For polydisperse systems, one may in principle *determine the polydispersity index*.

- For *non-ideal solutions* one may determine *thermodynamic interactions*, e.g. A_2 and A_3.

- The *biggest drawback* of equilibrium centrifugation is associated with the *long time* (several days) it takes the system to reach equilibrium in the centrifuge.

INTRODUCTION OF "SCALING"

Concentration regions and concentration fluctuations

in polymer solutions

Dilute   Semidilute   Concentrated
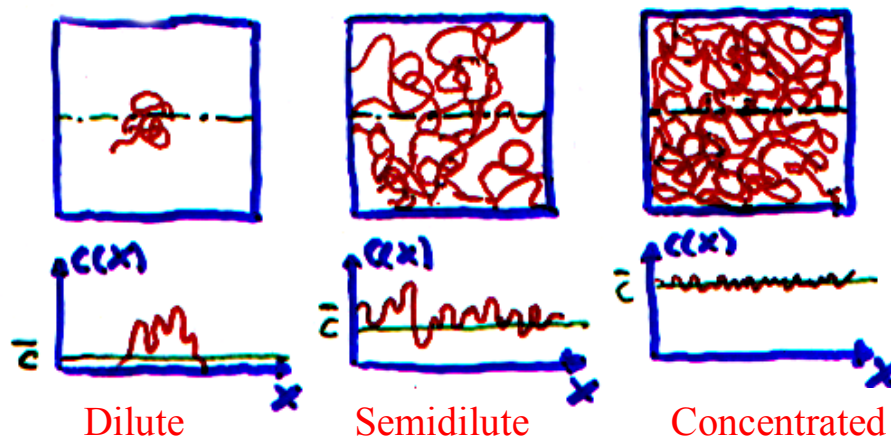
Dilute solutions:

The polymer molecule behaves as *separate entities*

without intermolecular interactions.

Characteristic parameters: R_G, R_D and $[\eta]$.

Static parameter:

$$R_G = K_G \cdot M^{\beta_G}$$

$\beta_G = 0.59$ (good conditions)
$\beta_G = 0.50$ (θ-conditions)

Dynamical parameters:

$$D_0 = \frac{R \cdot T}{N_A \cdot f_0}$$

$$D_0 = \frac{k \cdot T}{f_0} = \frac{k \cdot T}{6\pi \cdot \eta_0 \cdot R_D}$$

Stoke's law:

$$f_0 = 6\pi \cdot \eta_0 \cdot R_D \; ; \; R_D = K_D \cdot M^{\beta_D}$$

At *θ-conditions*, we always have $\beta_G = \beta_D$.

At good conditions: $\beta_G = \beta_D$ only when $M \to \infty$,

otherwise: $\beta_D < \beta_G$ and the numerical value of β_D *is*

dependent on the considered molecular weight region.

Intrinsic viscosity:

$$[\eta] = k \cdot M^a$$

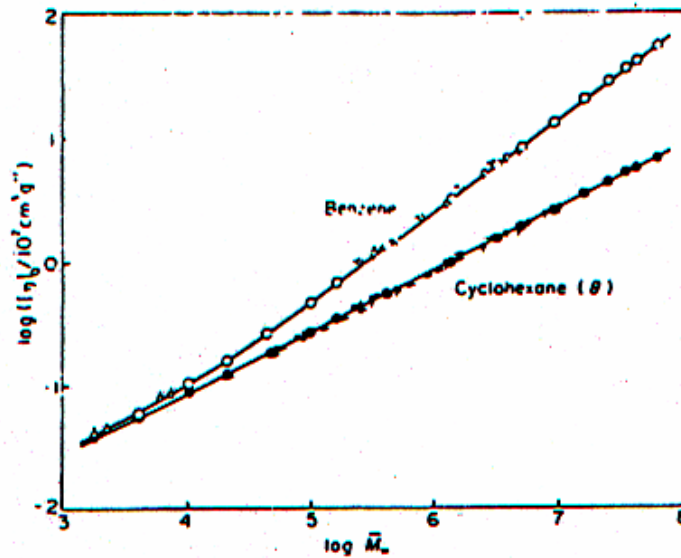$$[\eta] \propto \frac{R_D \cdot R_G^2}{M} \propto M^{2\beta_G + \beta_D - 1}$$

Fig. 5. Relation between zero-shear-rate intrinsic viscosity $[\eta]_0$ and weight-average molecular weight $\bar{M}_w$ for polystyrene in benzene at 25 or 30°C and in cyclohexane at the theta temperature. (O, ●) present data; (Ó, ♦) Altares et al. (ref. 8); ●, Berry (ref. 9); (φ, ♥) Fukuda et al. (ref. 7); (Ю, ─●) Yamamoto et al. (ref 10).

Semidilute solutions:

In this concentration region, the *intermolecular*

interactions are dominating.

At a certain concentration, c*, ("overlap concentration") *the polymer molecules starts to overlap with each other*, and a *transient network* is formed.
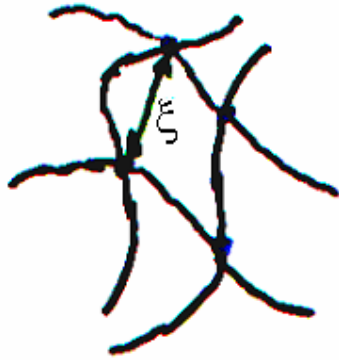
Static experiments:

$$c^* \propto \frac{M}{R_G^3} \propto M^{1-3\beta_G}$$

$c^* \propto M^{-0.76}$ (good conditions)

$c^* \propto M^{-0.50}$ (θ-conditions)

Dynamical experiments:

$$c^* = \frac{1}{[\eta]} \propto M^{1-2\beta_G-\beta_D}$$

Part of a network.

This network is characterized by a "*correlation length*" ("screening length"), ξ, that are *independent of the molecular weight of the polymer*, but *dependent of the concentration of the solution*.

$$\xi \propto c^x \text{ where } x \equiv \frac{\beta_G}{1 - 3 \cdot \beta_G}$$

$\xi \propto c^{-0.77}$ (good conditions)

$\xi \propto c^{-1.0}$ (θ-conditions)

Scaling laws in the *semidilute region* is based on the existence of an *overlap concentration,* c*, where *the concentration dependence* of a given parameter (Π, S, D) *is changing*.

In addition to the existence of a *correlation length*, ξ, that are *dependent on the polymer concentration*, but *independent on the molecular weight of the polymer*.
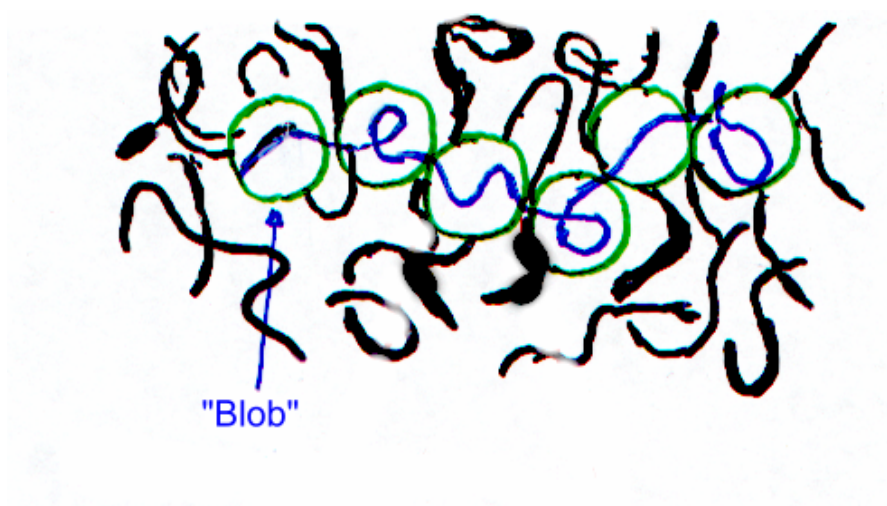
Concentrated solutions

A *homogenous distribution of segments* in the solution. At a concentration, c^{+}, the *chain dimensions will be independent of the concentration* and assume their *non-perturbed dimensions*. (c>15 %); $c^{+} = \dfrac{6}{[\eta]_{\theta}}$.

Illustration of characteristic lengths and concentration regions
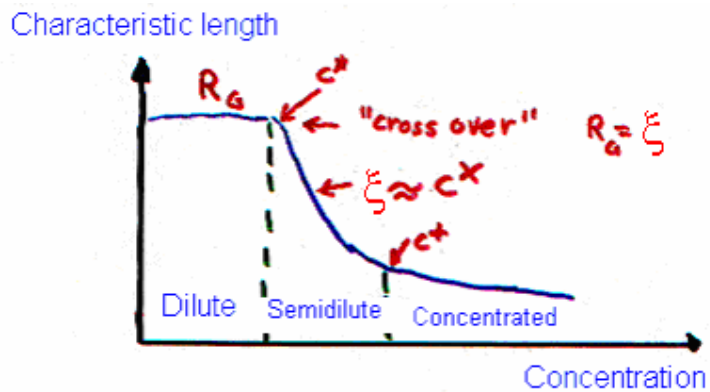
Description of semidilute polymer solutions with the aid of the "Blob" model.

A *semidilute solution* may be considered to consist of a *string of "blobs"* of the size ξ. Each "blob" has the molecular weight ($\xi_G \propto c^{\beta/(1-3\beta)}$)

$$M(\xi) \propto c \cdot \xi_G^3 \propto c^{\frac{1}{1-3\cdot\beta}}$$

Phenomenological consideration of osmotic pressure, diffusion and sedimentation with the aid of Scaling-laws

Osmotic pressure:

$$\Pi = \frac{R \cdot T}{M} \cdot \left(c + A_2 c^2 + A_3 c^3 + \cdots \right)$$

"Mean field" (Flory):

$\Pi \approx c^2$ (good conditions)
$\Pi \approx c^3$ (θ-conditions)

"Scaling":

$$\frac{\Pi}{c} = \frac{R \cdot T}{M_{"blob"}}$$

$$\Pi \propto \frac{c}{c \cdot \xi^3}$$

$$\Pi \propto c^{-\frac{3\beta_G}{1-3\beta_G}}$$

We set $\beta_G = 0.59$

$\Pi \propto c^{2.31}$ (good conditions)

$\Pi \propto c^3$ (θ-conditions)

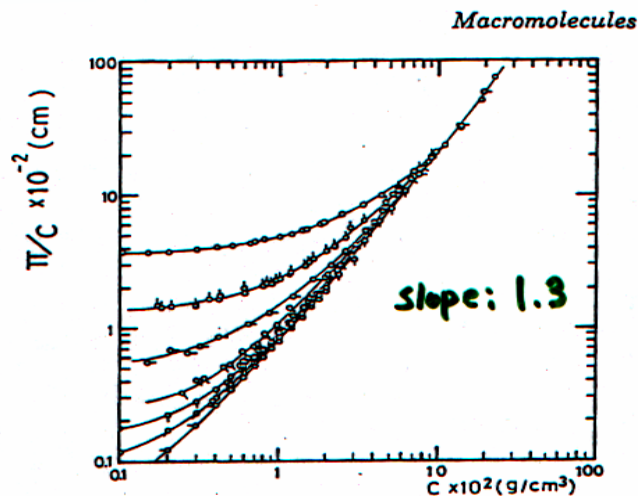Figure 4. Osmotic pressures of poly(α-methylstyrenes) in toluene at 25 °C. The symbols O, Ó, O, Q, Q, O, and O denote data for α-104, α-12, α-103, α-110, α-112, α-113, and α-111, respectively. The data for α-112 were obtained by both osmotic pressure and light scattering measurements, and the data for α-113 and α-111 were obtained by light scattering measurements.

In order to simplify the analysis of diffusion- and sedimentation data, we assume: $M \to \infty$, then

$\beta_G = \beta_D = \beta$ and $\xi_G = \xi_D = \xi$.

Diffusion (cooperative):

$$D = \frac{k \cdot T}{6\pi \cdot \eta_0 \cdot \xi} \propto \xi^{-1}$$

$$D \propto c^{-\frac{\beta}{1-3\cdot\beta}}$$

$D \propto c^{0.77}$ (good conditions)
$D \propto c^{1.0}$ (θ-conditions)

Sedimentation (cooperative):

$$S = M \cdot \frac{1 - v_2 \cdot \rho}{N_A \cdot f} \propto \frac{M_{\text{"blob"}}}{6\pi \cdot \eta_0 \cdot \xi} \propto \frac{c \cdot \xi^3}{6\pi \cdot \eta_0 \cdot \xi} \propto c \cdot \xi^2 \propto c^{1+\frac{2\beta}{1-3\beta}}$$

$$S \propto c^{\frac{1-\beta}{1-3\beta}}$$

$S \propto c^{-0.53}$ (good conditions)
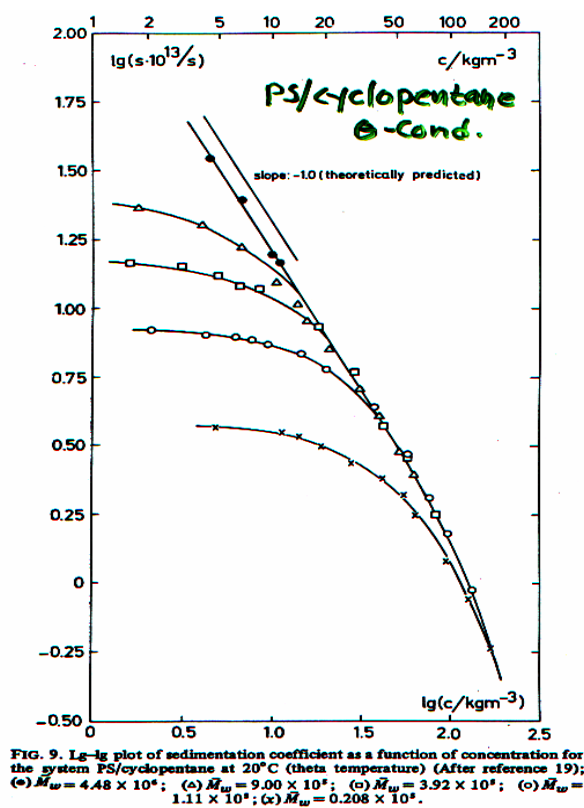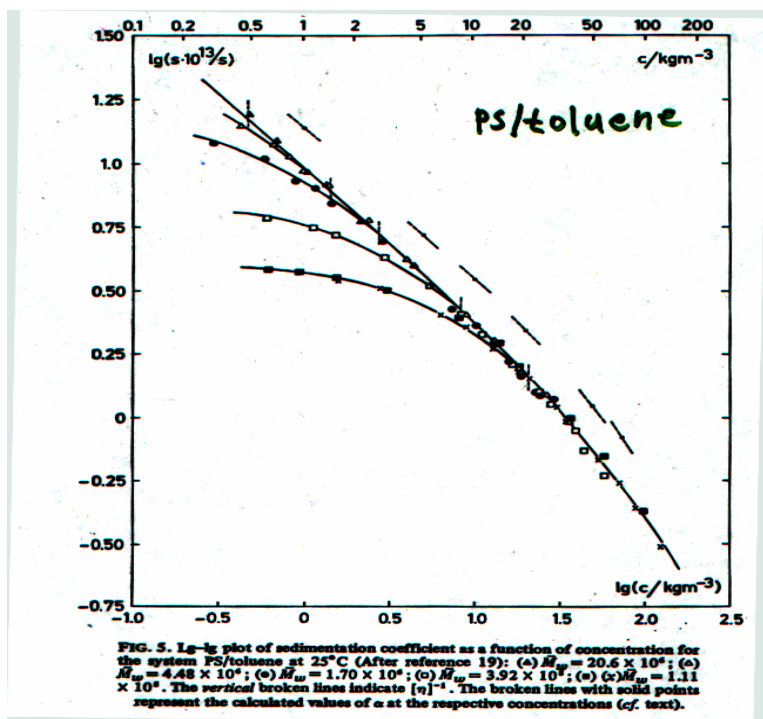$S \propto c^{-1.0}$ (θ-conditions)

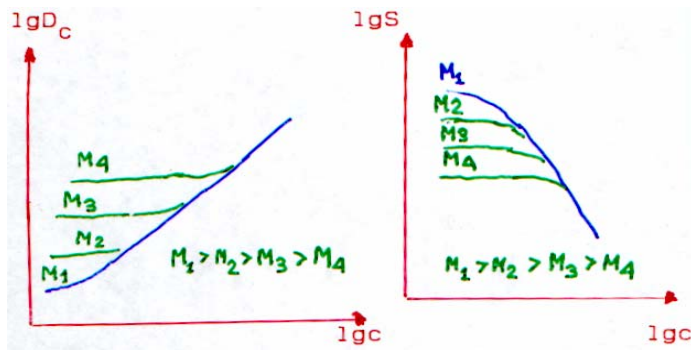FIG. 5. Lg–lg plot of sedimentation coefficient as a function of concentration for the system PS/toluene at 25°C (After reference 19): (△) $\bar{M}_w = 20.6 \times 10^6$; (▲) $\bar{M}_w = 4.48 \times 10^6$; (●) $\bar{M}_w = 1.70 \times 10^6$; (○) $\bar{M}_w = 3.92 \times 10^5$; (□) $\bar{M}_w = 1.11 \times 10^5$. The *vertical* broken lines indicate $[\eta]^{-1}$. The broken lines with solid points represent the calculated values of α at the respective concentrations (*cf.* text).

FIG. 9. Lg–lg plot of sedimentation coefficient as a function of concentration for the system PS/cyclopentane at 20°C (theta temperature) (After reference 19); (●) $\bar{M}_w = 4.48 \times 10^6$; (△) $\bar{M}_w = 9.00 \times 10^5$; (□) $\bar{M}_w = 3.92 \times 10^5$; (○) $\bar{M}_w = 1.11 \times 10^5$; (x) $\bar{M}_w = 0.208 \times 10^5$.
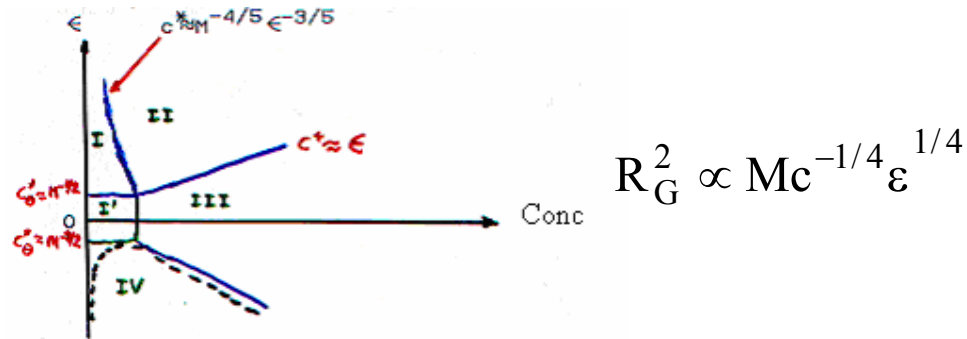
Temperature-concentration diagram

"Mean field" theory
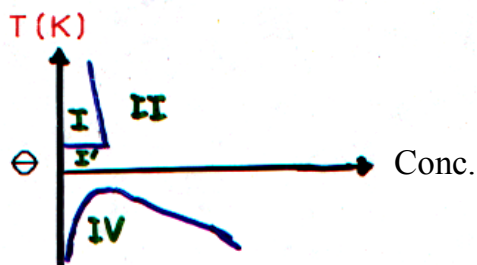
I. *Dilute solution and good thermodynamic conditions*

II. *Semidilute and concentrated solutions at good conditions*

I'. *θ-region*

IV. *Phase separations curve*

Reduced temperature: $\varepsilon = \dfrac{T - \theta}{\theta}$

$$R_G^2 \propto Mc^{-1/4}\varepsilon^{1/4}$$

I.   *Dilute concentration regime*

The I and II is separated by the overlap concentration

$$c^* \propto \dfrac{M}{R_G^3} \qquad\qquad c^* \propto M^{-\frac{4}{5}} \cdot \varepsilon^{-\frac{3}{5}}$$

I'. *Dilute θ-region*

The function $c_\theta^* \approx M^{-1/2}$ separates the θ-region from the dilute region (good conditions) (I) and the θ-region from the phase separation region (IV).

II. *The semidilute regime*

III. *The concentrated regime*

IV. *Phase separation region*

RHEOLOGY AND THE MECHANICAL PROPERTIES OF POLYMERS

Rheology:

i)   *Viscous flow* - irreversible deformation

ii)   *Rubber elasticity* - reversible deformation

iii)   *Viscoelasticity* - the deformation is reversible, but time dependent

iv) *"Hookean" elasticity* - the motion of the chain segment is very restricted, but involves bound stretching and bound angle deformation
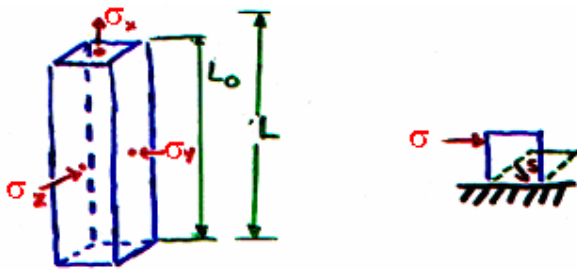
Polymers
{
Crystalline – first order transition (ice-water)

Amorphous – chains that cannot be arranged in an ordered way
}

"Glass"-rubber transitions

Simple mechanical relations:

Young's-modulus:

This modulus describes the coupling between *elastic and viscous properties* of a polymer system.

For *elastic behavior* of flexible polymer chains, the *shear stress* is

$$\sigma = \frac{F}{A}$$

related to *the stretching*

$$\varepsilon = \frac{L - L_0}{L_0}$$ by the following equation:

$$\sigma = E \cdot \varepsilon \qquad (79)$$

where E is called *Young's elasticity modulus*.

This *modulus* gives information of the *stiffness of the polymer*. The higher E, the greater tendency the polymer material has to *resist stretching*.

Ex.

Material	E (Pa)
copper	$1.2 \cdot 10^{11}$
polystyrene	$3 \cdot 10^9$
soft rubber	$2 \cdot 10^6$

Shear modulus:

$$G = \frac{\sigma}{s}; \; s = \text{shear deformation (shear angle)}$$

Newton's law: The equation for an ideal liquid with viscosity η, may be written as:

$$\sigma = \eta \cdot \frac{ds}{dt} \qquad\qquad (80)$$

$$\frac{ds}{dt} = \text{shear deformation rate}$$

Equ. (80) describes the viscosity for simple liquids at *low flow rates*.

Compliance and modulus

The modulus measures the stiffness or hardness for an object, while the *compliance, J, measures the softness*. The elastic compliance is defined in the following way:

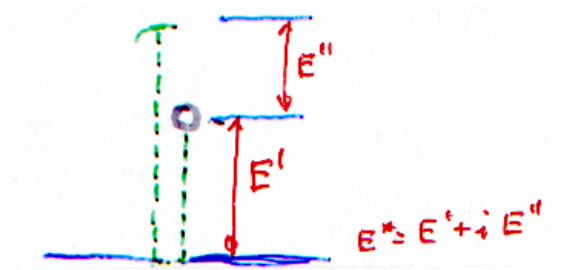$$J = \frac{1}{E}$$
(81)

Storage- and loss moduli
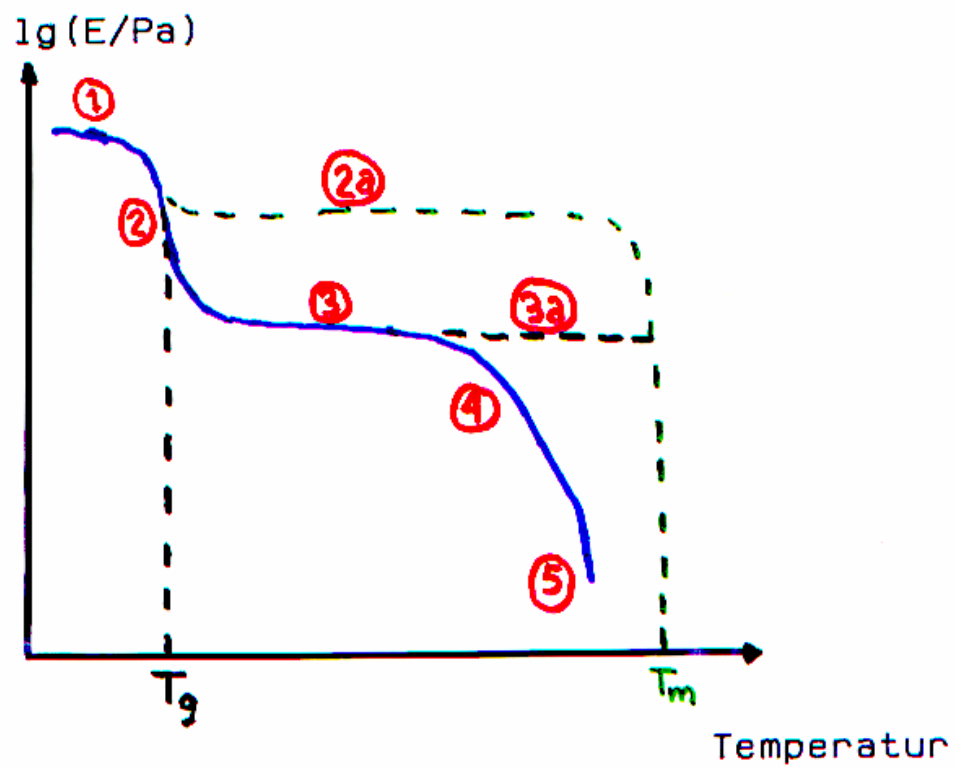
The complex Young's modulus:

$$E^* = E' + iE''$$

E' = real part; iE'' = imaginary part;

E'= storage modulus   E'' = loss modulus.

E' is a measure of the *elastic energy* that is stored under deformation, and E'' is a measure of the *energy that is converted to heat*.

$$E^{*} = E' + i\, E''$$

The Young-Modulus' temperature dependence

(1) *The glass region:*

Ex. PS and PMMA at 25 °C. *Here E is approximately constant.* The size of E is often ca. $3 \cdot 10^9$ Pa. The molecular motion is *limited to vibrations and short distance rotations*.

(2) *The glass transition region:*

In this region *E often decreases with a factor of 1000* over a temperature region of 20-30 °C. The *stiffness of the polymer changes quite rapidly* in this region. T_g $\left(\dfrac{d^2E}{dT^2} \text{ maksimum} \right)$ is the *glass transition temperature* and represents the transition from *"glass"- to rubber-like behavior*.

This region (2) may, from a molecular view, be described as *long-range coordinated molecular motion*. At temperatures under the glass transition only *1-4 chain atoms are involved in motions*, while at temperatures in the glass transition region *10-50 chain atoms are involved in a correlated motion*.

Ex.	Polymer	T_g (°C)	Number of chain atoms
	PDMS	127	40
	PS	100	40-100
	polyisoprene	-73	30-40

(2a)   Illustrates the *effect of crystallinity*. T_m is the melting point of the polymer.

(3) *Rubber plateau region:* In this region, *E is approximately constant* ($2 \cdot 10^6$ Pa). In this region, the polymer exhibits *rubber elasticity*

i) Linear polymer: *The extent* of the plateau region will primarily depend on the *polymers molecular weight*.
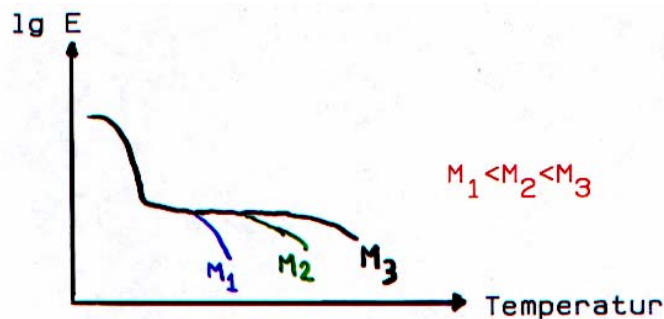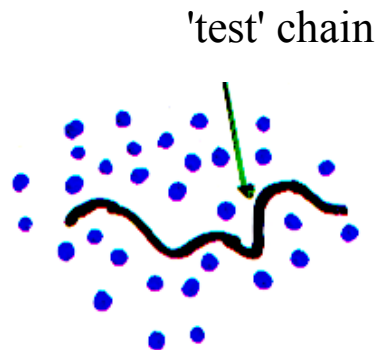

ii) Cross-linked polymer (3a)

Cross-linking gives "better" rubber elasticity.

$E = 3 \cdot n \cdot R \cdot T$; n = number of active chain segments.

In region (3) the *molecular motion* may be described by *"reptation"*.

'test' chain

(4) *Rubber flow region:* In this region, the polymer has both *rubber-elastic and flow properties, dependent on which time scale* the process is regarded on.

i)*Short times*: The physical "entanglements" do not have time to relax (rubber)

ii)*Long times*: The chains move in a coordinated way (flow).

(5) *The liquid flow region:* Here the polymer exhibits

flow properties $\sigma = \eta \cdot \dfrac{ds}{dt}$ at ideal conditions. This

region may also be describes by the *"reptation"*

model.

Viscous flow: $\sigma = \eta \cdot \dfrac{ds}{dt}$

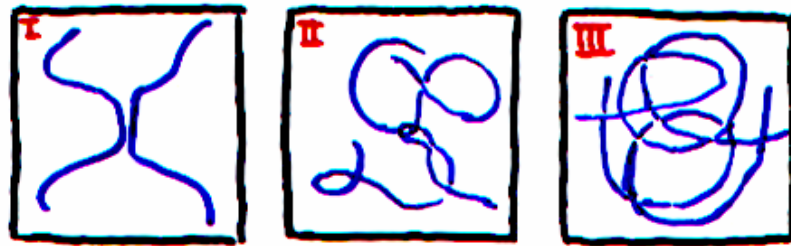σ = shear stress; $\dfrac{ds}{dt}$ = the shear deformation rate

THE MOLECULAR WEIGHT DEPENDENCE OF
THE VISCOSITY

At *molecular weights lower* than the *"entanglement"*

molecular weight (M_E): $\eta \propto M^{1.0}$

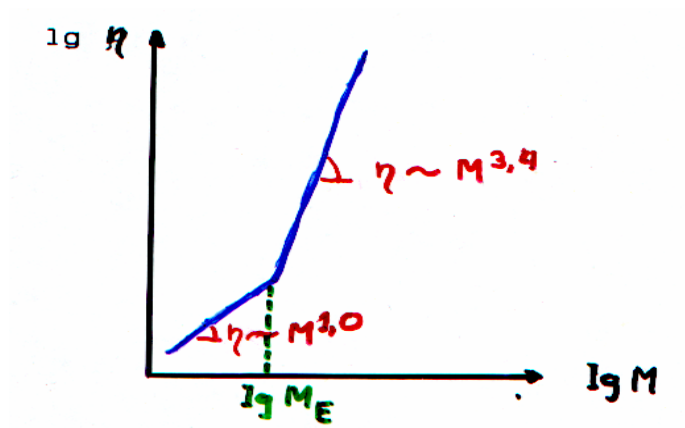*Illustration of different" entanglement"*

situations

I.   Temporary "cross-link"

II. Local "link"

III. "Looping" of chains around each other in the form

of long-distance contour

$M_E^{PS} \approx 37000; \quad M_E^{PMMA} \approx 10000; \quad M_E^{PEO} \approx 6000$

For molecular weights over M_E: $\eta \propto M^{3.4}$

The graph shows $\lg \eta$ versus $\lg M$ with annotations:
$\eta \sim M^{3,4}$ (upper region)
$\Delta \eta \sim M^{1,0}$ (lower region)
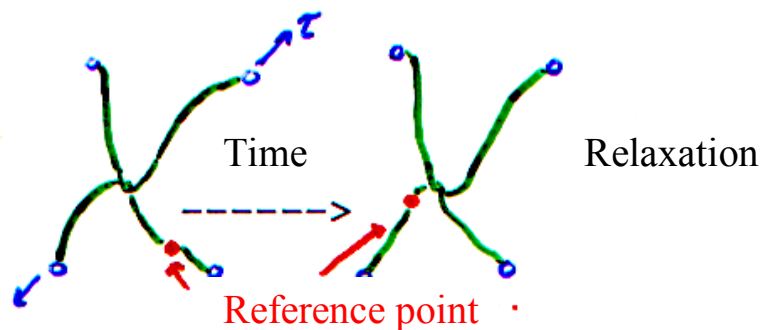$\lg M_E$ at the transition point.

Time dependent viscosity effects:

"Thixotropic" liquid: the viscosity decreases with time

"Rheopectic" liquid: the viscosity increases with time

Viscoelasticity and models for stress relaxation:

Time ⟶   Relaxation

Reference point

$\sigma = E \cdot \varepsilon$ (elastic tress)

σ = shear stress

E = Young's modulus

ε = tension
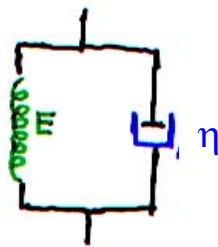
$\sigma = \eta \cdot \dfrac{d\varepsilon}{dt}$ (viscous stress)

Voigt model: $\sigma = \sigma_{elastic} + \sigma_{viscous} = E \cdot \varepsilon + \eta \cdot \dfrac{d\varepsilon}{dt}$

Maxwell model: $\quad \dfrac{d\varepsilon}{dt} = \left(\dfrac{d\varepsilon}{dt}\right)_{elastic} + \left(\dfrac{d\varepsilon}{dt}\right)_{viscous}$

$$\dfrac{d\varepsilon}{dt} = \dfrac{1}{E} \cdot \dfrac{d\sigma}{dt} + \dfrac{\sigma}{\eta}$$

Voigt modell   Maxwell modell

E = elastic element (spring)

η = viscous element (damping cylinder)

In viscoelastic measurements, on may follow a *transient- or "steady-state"-response*. Two common transient experiments are *stress relaxation and creeping*.

Stress relaxation:

A *rapid external stress* is applied at the time $t = 0$ and the relaxation is measured as a *function of time*. The *Maxwell model is suitable* to describe this:

ε = start tension = constant at the time $t = 0$.

Thereafter $\dfrac{d\varepsilon}{dt} = 0$.

$$\frac{1}{E} \cdot \frac{d\sigma}{dt} + \frac{\sigma}{\eta} = 0$$

$$\sigma = \sigma_0 \cdot \exp(-\frac{E \cdot t}{\eta})$$

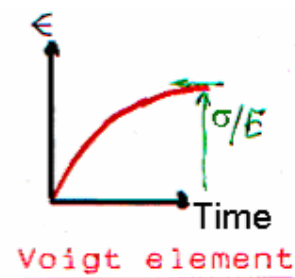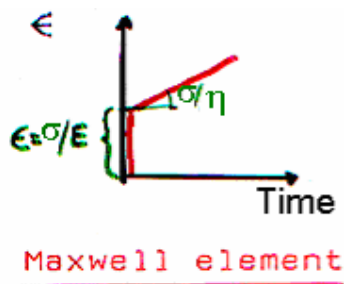The relation $\dfrac{\eta}{E}$ is a constant with the dimension time,

and is called relaxation time, τ_r

$$\boxed{\tau_r = \frac{\eta}{E}}$$ 　　　　　　　　(82)

If η *is large*, the relaxation time is long, and the *stress*

relaxes slowly.

One often defines the *relaxation time* as the time it

takes for the *stress to relax to* $\dfrac{1}{e}$ *of its start value*.

Maxwell element　　　　　　Voigt element

Creep: In this experiment a *constant external strain is applied at the time t = 0*. The deformation is measured as a function of time by keeping the stress constant. *To describe creep, Voigt's model is often used*: The stress is constant $\sigma = \sigma_o$.

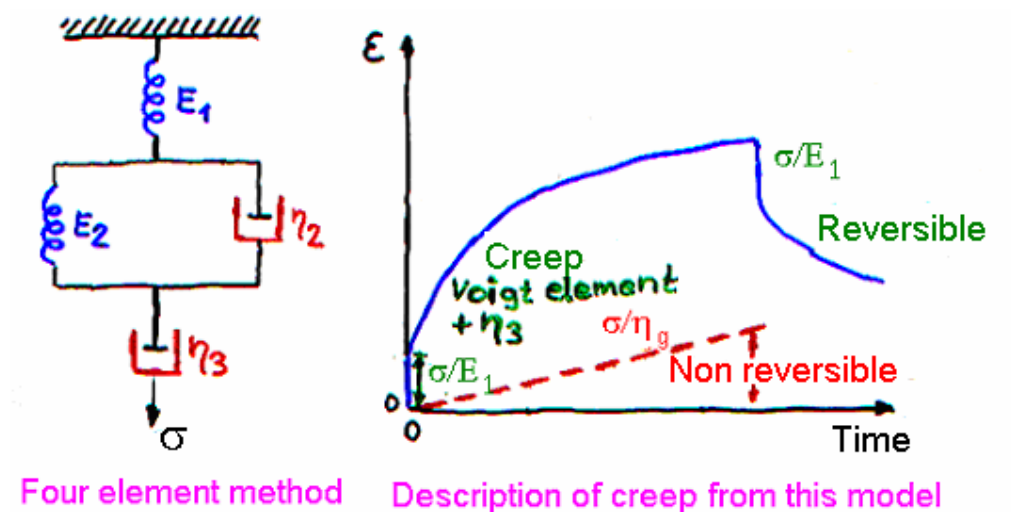$$\sigma_0 = E \cdot \varepsilon + \eta \cdot \frac{d\varepsilon}{dt} \tag{83}$$

$$E \cdot \frac{\varepsilon}{\sigma_0} = 1 - \exp\left(-\frac{E \cdot t}{\eta}\right) \tag{84}$$

The ratio $\frac{\eta}{E}$ is called the *retardation time* of a *creep experiment*.

The four-element model

This model that consists of *four elements*, may be used to describe many practical applications

$$\varepsilon = \frac{\sigma}{E_1} + \frac{\sigma}{E_2} \cdot (1 - e^{-\frac{t}{t_\eta}}) + \frac{\sigma}{\eta_3} \cdot t$$


Four element method   Description of creep from this model

RUBBER ELASTICITY

The natural material rubber $(C_5H_8)_n$ (isoprene)

The following three conditions must be fulfilled for a material to *exhibit rubber properties*:

1) It has to consist of *long chain molecules* with bounds that permit *free rotation*

2) *The forces* between the molecules *must be weak* as in a liquid

3) *The molecules* must be connected, *cross-linked*, at certain points along the chains
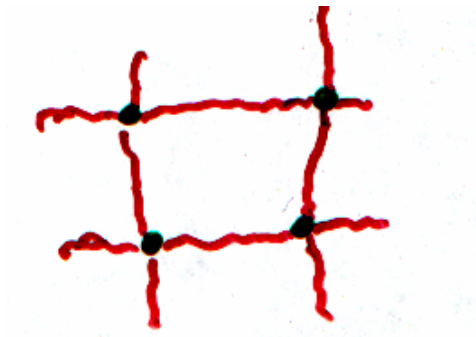
Elastomers (rubber) may, over their glass transition temperature, be defined as an *amorphous cross-linked polymer*.
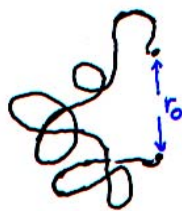
The stress for an elastomer may be described in the following way:

$$\sigma = n \cdot R \cdot T \cdot (\alpha - \frac{1}{\alpha^2})$$

L_0 = the distance from the start

$$\alpha = \frac{L}{L_0}$$

$$n = \frac{\rho}{M_c} = \frac{\text{density}}{\text{molecular weight}} \quad \text{between cross-links}$$

n represents the number of "active" network segments pr. unity volume.

THERMODYNAMICS FOR RUBBER ELASTICITY

When one talks about *equilibriums in systems that changes in a reversible way* (e.g. elastic deformation), it is practical to introduce *Helmholtz free energy, A,* defined by:

A = U - T·S; U = inner energy   (85)

The *backward-pulling force, f,* which operates on the elastomer, is dependent on the change in free energy when the distance is changed:

$$f = \left(\frac{\partial A}{\partial l}\right)_{T,V} = \left(\frac{\partial U}{\partial l}\right)_{T,V} - T \cdot \left(\frac{\partial S}{\partial l}\right)_{T,V} \qquad (86)$$

For an *ideal elastomer*:

$$\left(\frac{\partial U}{\partial l}\right)_{T,V} = 0$$

for most other materials (e.g. a steel rod):

$$T \cdot \left(\frac{\partial S}{\partial l}\right)_{T,V} = 0$$

One may show that there is a direct *correlation*

between the entropy and f:

$$-\left(\frac{\partial S}{\partial l}\right)_{T,V} = \left(\frac{\partial f}{\partial T}\right)_{l,V} \qquad (87)$$

This leads to the *state equation for rubber elasticity*

$$f = \left(\frac{\partial U}{\partial l}\right)_{T,V} + T \cdot \left(\frac{\partial f}{\partial T}\right)_{l,V}$$

(88)

The first term on the right side in the equ. (88)

represents the *energetic part* (f_e) and the second term

is a *entropy part* (f_s): $f = f_e + f_s$