Viscoelasticity of Polymer Fluids.
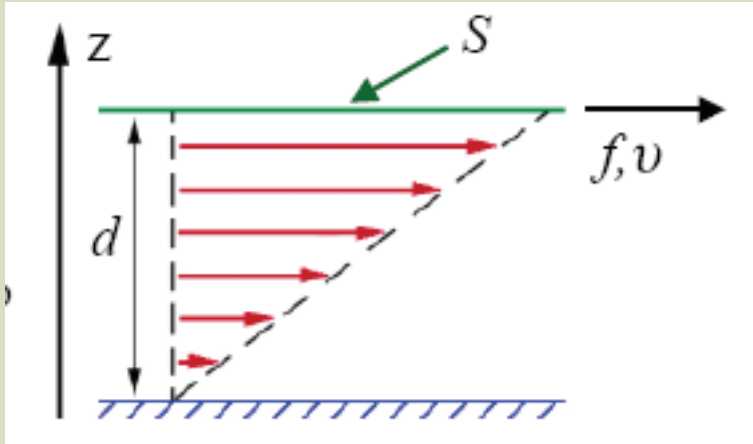
Main Properties of Polymer Fluids.

Entangled polymer fluids are polymer melts and concentrated or semidilute (above the concentration $c*$) solutions. In these systems polymer coils strongly overlap with each other, and polymer chains are highly entangled.

These entangled polymer fluids have the following specific properties

(*i*) they normally have a very high viscosity;

(*ii*) these fluids keep for a long time the memory about the history of the flow;

(*iii*) the property of viscoelasticity: at fast (high frequency) external action the response is elastic, while for slow (low frequency) external action the response is viscous (i.e. the fluid starts flowing).

The Viscosity of Fluids.

Simplest setup for viscosity determination.

Newton-Stokes law:

$$f = \eta \, (S\upsilon)/d$$

The proportionlity coefficient η is called the viscosity of the fluid.

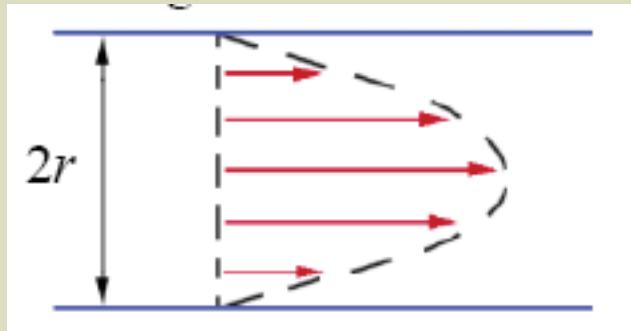In the differential form the Newton-Stokes law can be written as follows

$$\sigma = f/S = \eta(d\upsilon/dz)$$

where σ is imposed stress and z is the coordinate perpendicular to the plates.

Viscosity Measurements.

Viscosity is measured in poise: 1 poise = 1 g/ (cm sec).

The viscosity of water at room temperature is of order 10^{-2} poise, while viscosity of polymer melts can be of order 10^{10}- 10^{12} poise and even more.

Flow in capillary viscosimeter.
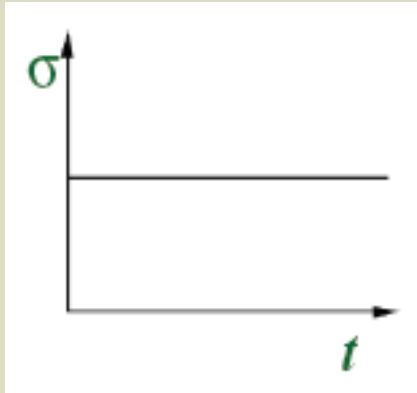
Viscosity is measured by viscosimeters. Most common are capillary viscosimeters.

The method of measurements is based on the Poiseille equation

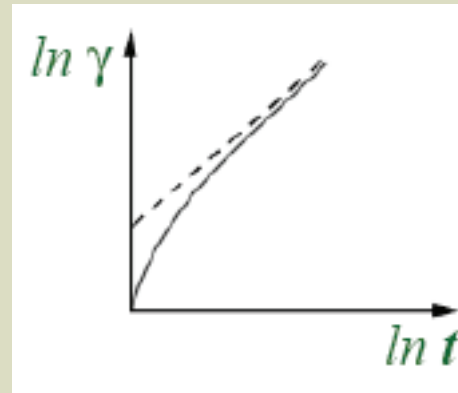$$Q = \frac{\pi r^4}{8} \frac{\Delta P}{\eta l} t$$

where Q is the mass of the fluid flown through the capillary during the time t, ΔP is the pressure difference at the ends of the capillary of length l and radius r.
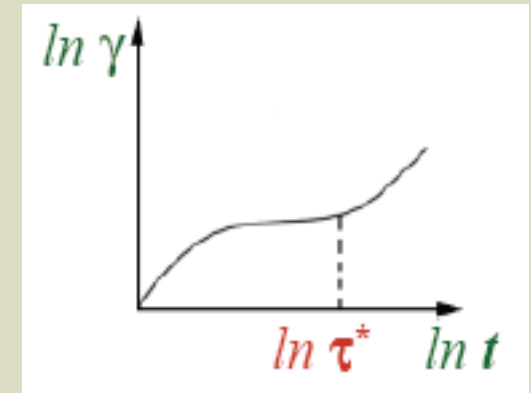
The Property of Viscoelasticity.

Step-wise stress starting at $t = 0$.

Reaction of an ordinary fluid.

Reaction of a polymer fluid.

The reaction of an ordinary fluid to such a stress would be a normal flow (after some initial equilibration period), i.e. the shear angle γ will vary with time as $\gamma = \sigma t/\eta$ where η is the viscosity of the fluid.

The typical reaction of polymer fluids is qualitatively different. At $\tau \ll \tau^*$ the value of $\gamma \simeq \sigma/E$ is practically constant and only at $\tau > \tau^*$ the flow starts: $\gamma \sim \sigma t/\eta$.

The Property of Viscoelasticity.

In other words, for entangled polymer fluids at $\tau \ll \tau^*$ there is an elastic response $\gamma \simeq \sigma/E$ where E is an effective Young modulus, while at $\tau \gg \tau^*$ we have $\gamma \simeq \sigma t/\eta$, i.e., the response is viscous. This is exactly the property of viscoelasticity.
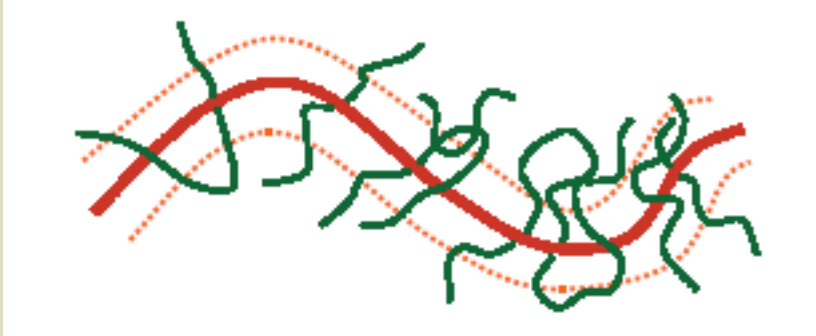
Comparing these two realtions, one gets

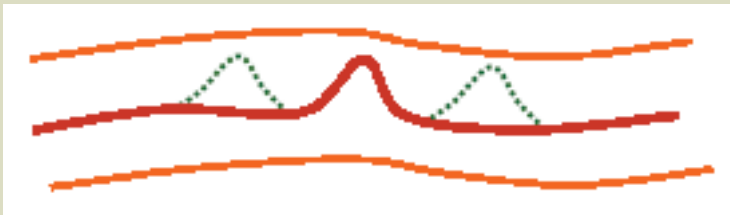$$\frac{1}{E} \sim \frac{\tau^*}{\eta} \qquad \text{or} \qquad \boxed{\eta \sim \tau^* E}$$

Viscoelasticity is a general property of all entangled polymer fluids, as long as they are not crystalline, glassy or crosslinked. Therefore, as for the property of high elasticity, the general molecular explanation should be possible which is based on the most fundamental properties of polymer liquids, i.e., the fact of the chain structure of polymer molecules, without the explicit reference to the specific chemical nature of monomer units.

Such explanation was developed by de Gennes, Doi an Edwards in 1970s, this theory is called theory of reptations.

Theory of Reptations.

Consider a chain entangled with many others and let us "freeze" for a moment the conformations of the other chains. This gives rise to a certain "tube": the given chain cannot escape in the directions perpendicular to the tube axis so that the only allowed type of motion is a snake-like diffusion along the tube axis. This kind of motion is called reptation:

Theory of Reptations.

If other chains are "unfrozen" the competing mechanism appears, that of "tube renewal", but it can be shown that reptations still always give a dominant contribution.

The neighboring chains which form the walls of the tube thus create restrictions for the motion of a given chain. In a sense, these restrictions are analogous to crosslinks.

However, these quasi-crosslinks have a final lifetime τ^*. Indeed, after some time the chain leaves the original tube and has an entirely new neighborhood.

We arrive, therefore, to the microscopic explanation of the phenomenon of viscoelasticity: if $t < \tau^*$ polymer liquid behaves as a network of quasi-crosslinks, and exhibits the elastic response to external stress, while at $t > \tau^*$ the quasi-crosslinks relax and the response is viscous.

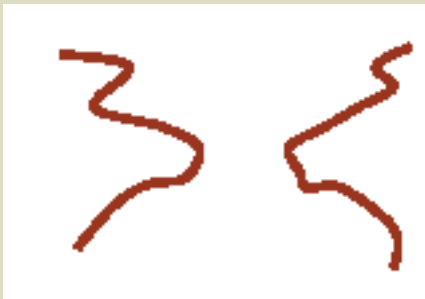# Distance between the Elastically Important Crosslinks.

What is the Young moudulus E for the network of crosslinks? According to the classical theory of high elasticity

$$E \sim kT\nu \sim kT/N_e a^3$$

where ν is the number of elastically active chains per unit volume, and N_e is the number of monomer units between two effective crosslinks.

It is usually assumed that N_e takes some constant value for each particular polymer, normally $N_e \sim 50 \div 500$, this is a phenomeno-logical parameter reflecting the fact that not all monomer-monomer contacts act like elastically important quasi-crosslinks:
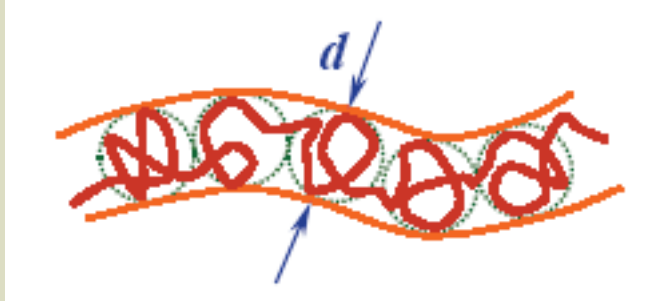

two neighbouing chains
not forming a crosslink

two neighbouing chains
forming a crosslink

Theory of Reptations. The Results.

schematic view of a reptation tube

The chain is a sequence of "blobs", each containing N_e links and having the size $d \sim N_e^{1/2} a$. The width of the tube is of the same order $d \sim N_e^{1/2} a$. The length of the tube is

$$\Lambda \sim \left(N/N_e \right) d \sim Na \big/ N_e^{1/2} \ll Na = L$$

The diffusion coefficient corresponding to reptation along the tube is $D_t = kT / \mu$, where μ is the corresponding friction coefficient; $\mu = N\mu_0$, and μ_0 is a friction coefficient for one monomer unit. Thus,

$$D_t = kT / N\mu_0$$

Theory of Reptations. The Results.

On the other hand, $\Lambda^2 \sim D_t \tau^*$, therefore

$$\tau^* \sim \frac{\Lambda^2}{D_t} \sim \frac{N^2 a^2 \mu_0 N}{N_e kT} \sim \frac{N^3}{N_e} \frac{\mu_0 a^2}{kT} \sim \frac{N^3}{N_e} \tau_0$$

where $\tau_0 = \mu_0 a^2 / kT \sim 10^{-12} \text{sec}$ is the characteristic microscopic time.

Note a very strong dependence on the chain length N: if $N \sim 10^5$ and $N_e \sim 10^2$ the relaxation time is of order $\tau^* \sim 10 \text{ sec}$, i.e., it is macroscopic. This is the reason of slow relaxation and high viscosity in polymer liquids. Thus

$$\eta \sim E\tau^* \sim \frac{kT}{N_e a^3} \frac{N^3}{N_e} \tau_0 \sim \frac{N^3}{N_e^2} \eta_0$$

where $\eta_0 \sim kT\tau_0 / a^3$ is a typical viscosity of a low molecular liquid which is of order of 1 poise.

Thus, theory of reptations predicts the dependence $\eta \sim N^3$ for polymer viscosity, which is rather close to the best fit of the experimental data $\eta \sim N^{3.4}$.

The Method of Gel-Electrophoresis.

Macromolecules containing charged monomer units are called polyelectrolytes. Charged monomer units appear as a result of dissociation reaction:

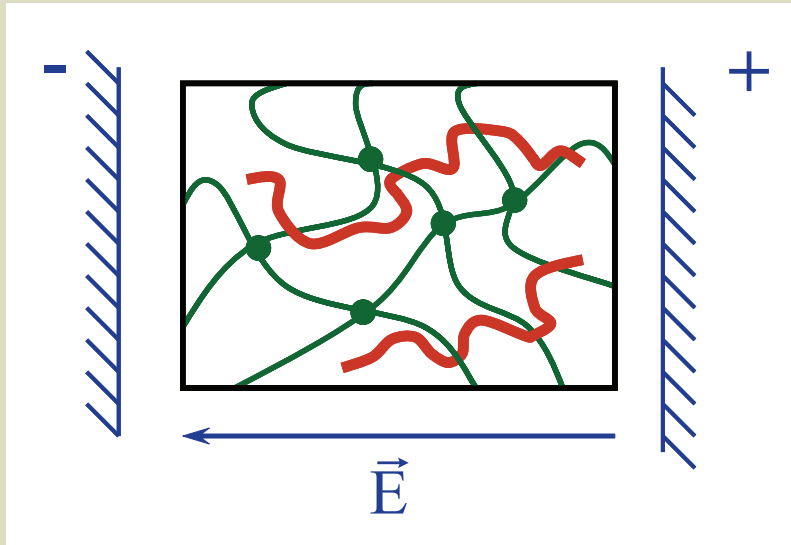neutral monomer unit $\rightleftarrows$ charged monomer unit + counter ion

The most important polyelectrolytes are biological macromolecules: DNA, RNA and proteins.

As an application of the reptation theory, let us consider the gel-electrophoresis of polyelectrolytes which is used to separate the polymer chains of different length and composition.

This method is most commonly used for the separation of the DNA fragments in the process of the so-called DNA sequencing.

The Method of Gel-Electrophoresis.

Gel is a swollen polymer network. The negatively charged DNA molecules (with total charge Q) move through the gel in external electric field E.

The drift velocity $\vec{\upsilon}$ depends on the chain length N. Therefore, the separation of the DNA molecules of different lengths is achieved.
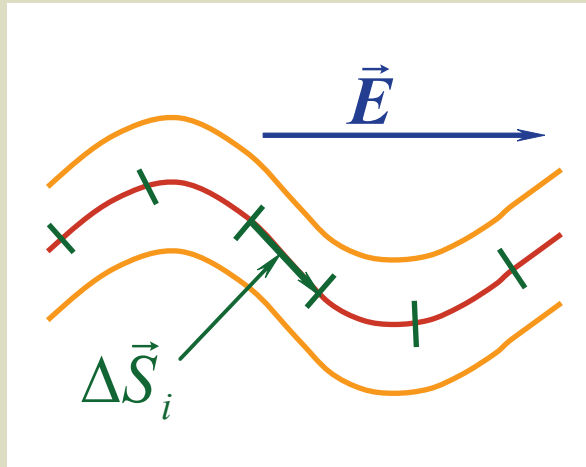
In the absence of a gel:

$Q\vec{E} = \vec{F}_{el} = \vec{F}_{fr} = \mu\vec{\upsilon}$, where μ is a friction coefficient. Thus,

$$\vec{\upsilon} = Q\vec{E}\big/\mu$$

But $Q \sim L$ and $\mu \sim L$ (the friction of the different parts of the DNA molecule adds up indepndently). Thus, velocity $\vec{\upsilon}$ does not depend on L and the DNA molecules do not separate in the solution.

The Method of Gel-Electrophoresis.

In the gel

DNA molecules are in effective "tubes" and move via reptations.

Let us divide the molecule in small fragments and count only the forces acting along the tube:

$$F_t = \sum_i \frac{Q\Delta\vec{S}_i}{L}\vec{E} = \frac{Q}{L}\left(\sum_i \Delta\vec{S}_i\vec{E}\right) = \frac{Q\vec{R}\vec{E}}{L}$$
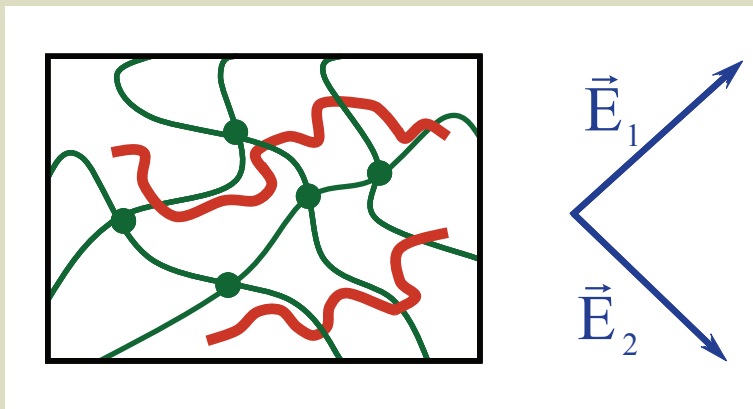
The drift velocity along the tube $\upsilon_t = F_t/\mu$, where $\mu = \mu_0 N$, and μ_0 is a friction coefficient of one monomer unit. Thus,

$$\upsilon_t = \frac{QRE}{L\mu_0 N}$$

Since $Q \sim L$ and $R \sim L^{1/2}$ (in weak field), the drift velocity $\upsilon_t \sim L^{-1/2}$, i.e., short chains move faster and the DNA fragments of different length do separate.

The Method of Gel-Electrophoresis.

Note however that in stronger fields the chains stretch, the end-to-end distance R becomes of order N, and the resolution of gel-electrophoresis vanishes. To solve this problem the direction of the field is turned by 90° back and forth after each interval τ^{*} (where τ^{*} is lower than the typical time of tube renewal).

Then the chain does not have time to stretch during one cycle. In this way it is possible to keep a good resolution of the method of DNA gel-electrophoresis even in rather strong fields.