UNESCO/IUPAC Postgraduate Course in Polymer Science

Lecture:

Polymer solutions in a nutshell

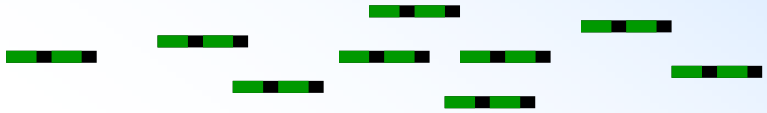
Jiří Horský

Institute of Macromolecular Chemistry ASCR, Heyrovsky sq. 2, Prague -162 06

http://www.imc.cas.cz/unesco/index.html

unesco.course@imc.cas.cz

Polymers



mononer

end groups

polymer

monomeric unit constitutional unit

polyethylene CH_2CH_2 CH_2

Polymers – under one name great variability

polymerization degree = number of monomeric units => molar mass/molecular weight (distribution, averages)

Architecture

HT HT HH TT HT

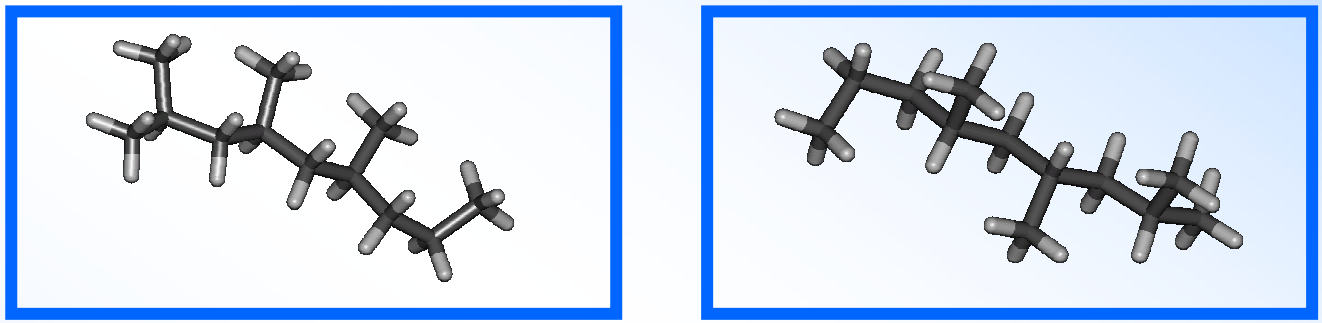
CH_2CH CH_2CH CH_2CH $CHCH_2$ CH_2CH CH_2CH

CH_3 CH_3 CH_3 CH_3 CH_3 CH_3

head-to-tail configuration (defects)

Stereoisomerism in the main chains

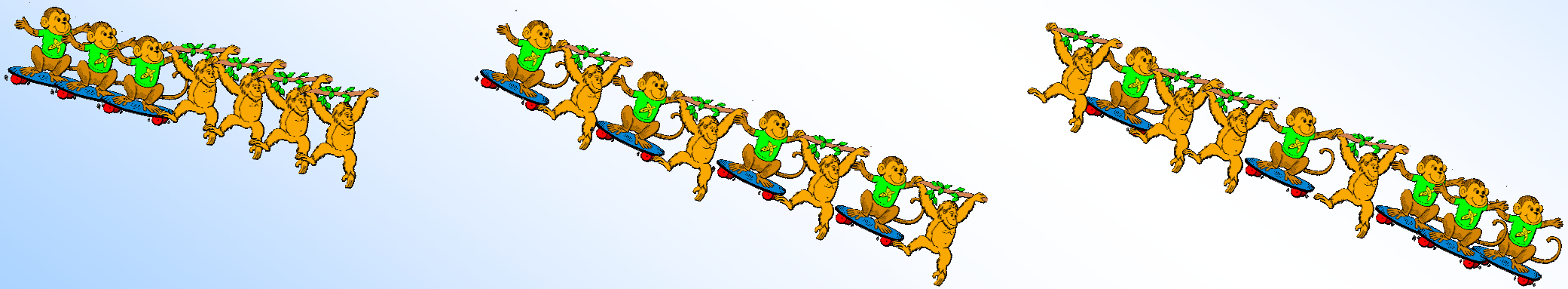
isotactic (meso) syndiotactic (racemic) atactic oligopropylene



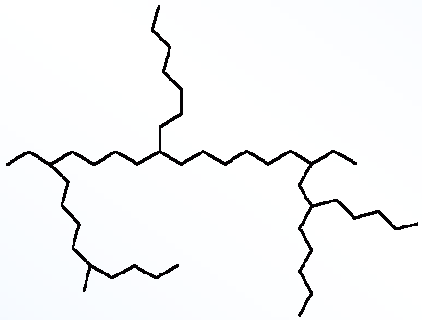
Substituents on the same side alternating the side random of zigzag chain

homopolymers, **copolymers,** terpolymers

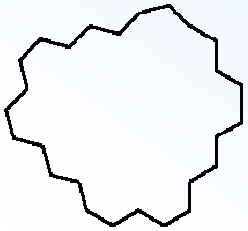
block alternating random/statistical



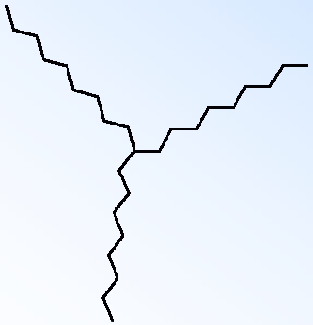
Non-linear macromolecules



short-chain/long-chain branched

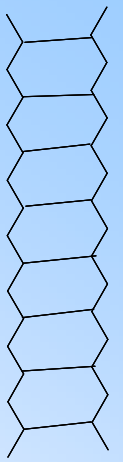


cyclic



(3 arm) star

comblike (graft)

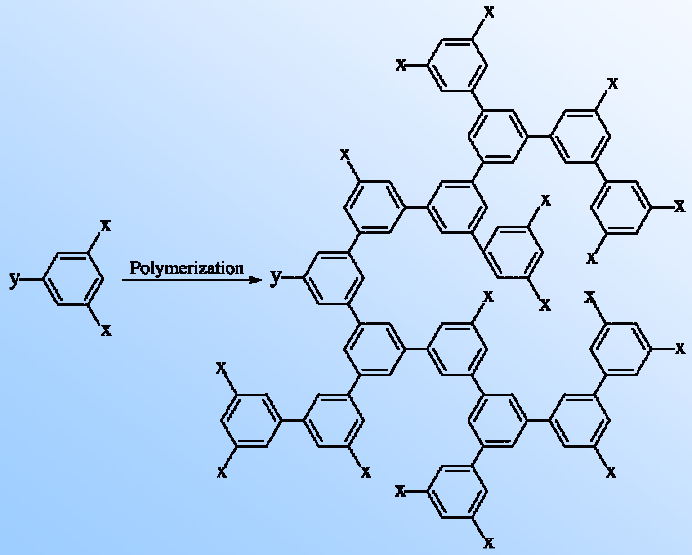


ladder

Special branching architectures

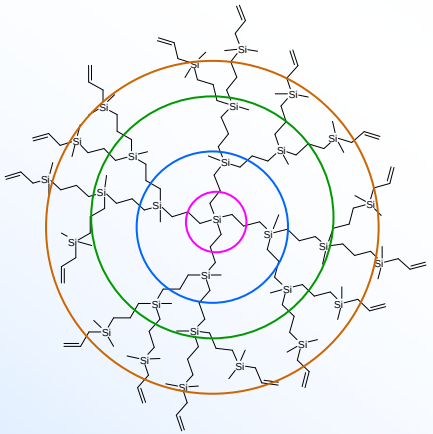
Hyperbranched polymers

one-step polycondensation of AB_n



Dendrimers

Two step reaction of AB_n – deprotection, extension



core
1. generation
2. generation
3. generation

carbosilane dendrimer

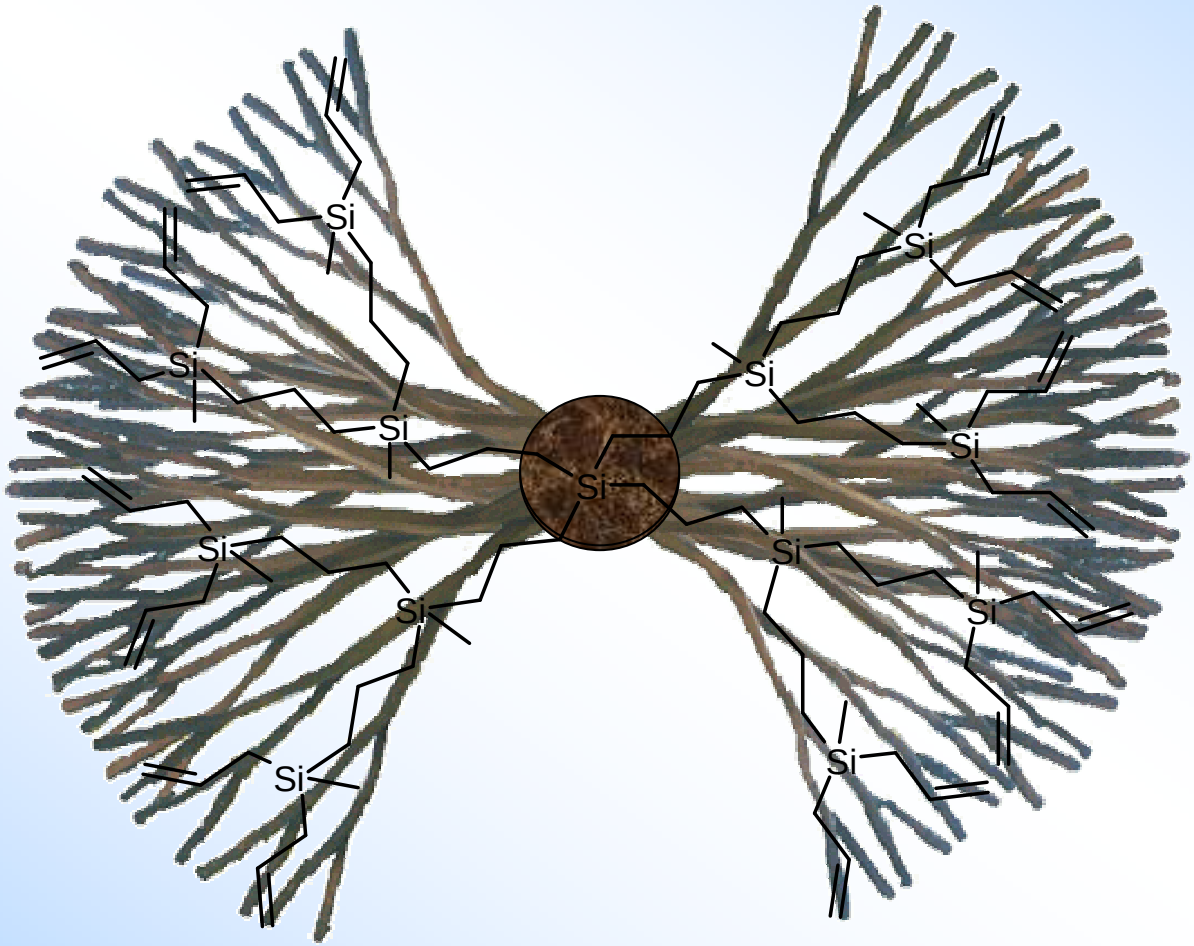
Prof. Otto Wichterle

Tree of knowledge

The statue
represents ever branching
macromolecular structures…

…

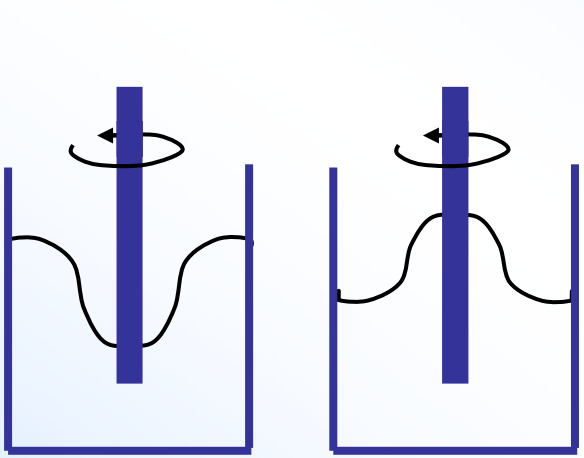
dendron



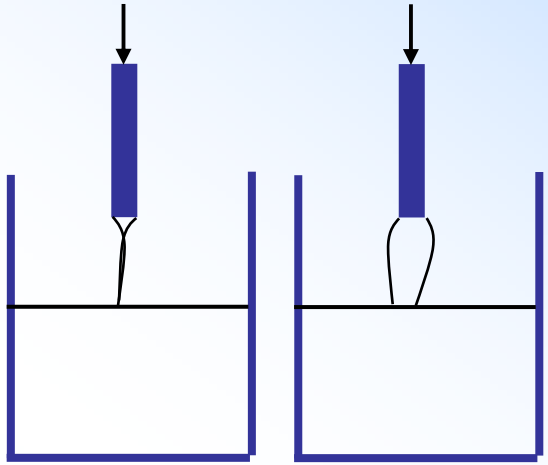
dendrimer

Fascinating polymeric liquids

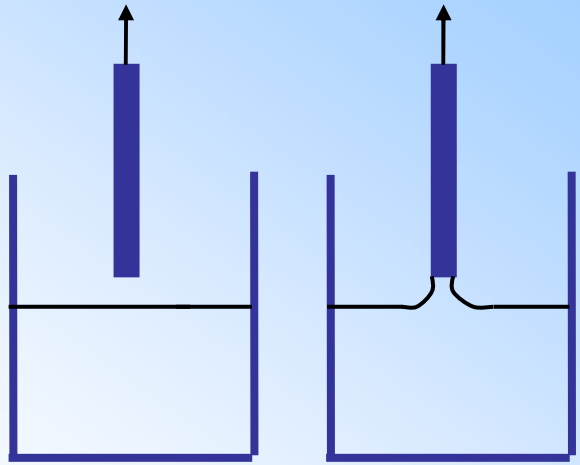
R. B. Bird and C. F. Curtiss Phys. Today **37**, 36 (1984)



climbing the rod



exit expansion



upward flow

Polymer solutions

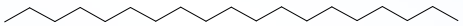
Applications (flow modifiers: paint, food, pharmaceutical industry etc.)
Life is solvent based (macromolecular schism-H. Morawetz, K.A. Dill)

structure/properties relation
structure -> properties (applications) properties -> structure (molecular characterization)

Flow properties (non-Newtonian liquids) thermodynamics radiation scattering

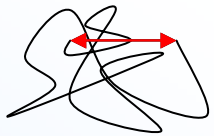
monodisperse linear homopolymer above its glass and melting temperatures

Isolated polymer molecule (infinite dilution) in inert solvent (vacuum)

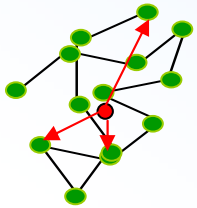


the extended zigzag conformation is just one from many possible ones => polymer coil

Size

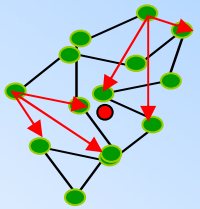


Bead and stick model



Root-mean-square radius of gyration

$$R_g^{\,2} = \left\langle \frac{\sum_{i=0}^{N} (r_i - r_g)^2}{N+1} \right\rangle = \frac{1}{2(N+1)} \left\langle \sum_{i=0}^{N} \sum_{j=0}^{N} (r_i - r_j)^2 \right\rangle$$



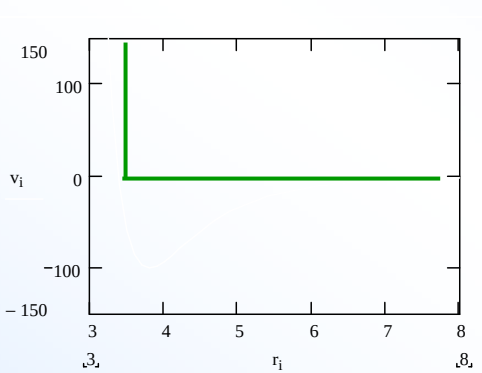
Root-mean-square end-to-end distance
$R_f^2 = \langle R^2 \rangle$ only linear molecules

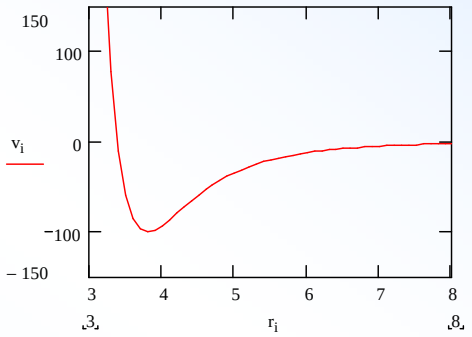
Not all conformation (combination of stick angles) are possible because beads cannot overlap
excluded volume between beads (monomeric units) distant along the chain (long-range)

Monomeric units/beads are not hard spheres

Interaction potential has attractive and repulsive part

The potential results from polymer/polymer, solvent/solvent and solvent /polymer interactions



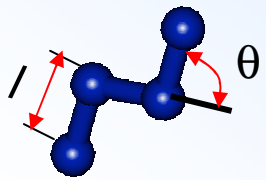


Under certain conditions repulsive and attractive parts compensate each other
$\Rightarrow$ effective zero volume (theta solvent, theta temperature)

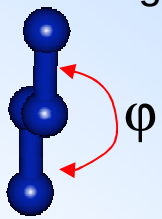
Ideal chain (zero excluded volume)

Variations of a bead-stick model

bond angle



dihedral angle



Freely-jointed chain: φ, θ free; *l* fixed

random walk $\Rightarrow$ binomial (normal for $n\to\infty$) distribution $\Rightarrow$ $R_f^2=nl^2$

Entropy elasticity $$f=\frac{\mathrm{d}G}{\mathrm{d}R}=\frac{\mathrm{d}}{\mathrm{d}R}(H-ST)=\frac{\mathrm{d}}{\mathrm{d}R}(-\mathrm{k}_b T\ln p(R))=\frac{\mathrm{d}}{\mathrm{d}R}(\frac{3}{2}\mathrm{k}_b T\frac{R^2}{R_f{}^2})=3\mathrm{k}_b T\frac{R}{R_f{}^2}$$

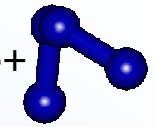
Freely rotating chain: φ free; θ (68°), *l (0.154 nm)* fixed $$R_f{}^2=nl^2\left(\frac{1+\cos\theta}{1-\cos\theta}\right)$$ (≅2)

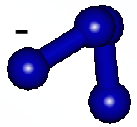
Hindered rotation model $$R_f{}^2=nl^2\frac{1+\cos\theta}{1-\cos\theta}\frac{1+<\cos\varphi>}{1-<\cos\varphi>}$$

Characteristic ratio $C_\infty=\dfrac{R_f{}^2}{nl^2}$

Rotational isomeric-state model
(interdependent rotation)

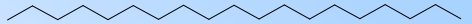
trans 

gauche+ 

gauche - 

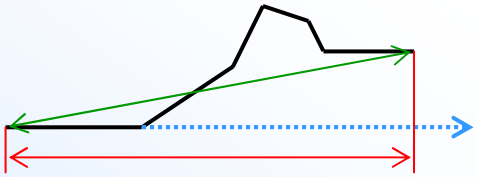
transfer matrix technique (Flory)

Equivalent freely jointed chain identical end-to-end distance $R_f^2=Nb^2$ and counter length $nl\ cos(\theta/2)=Nb$
b length of Kuhn segment



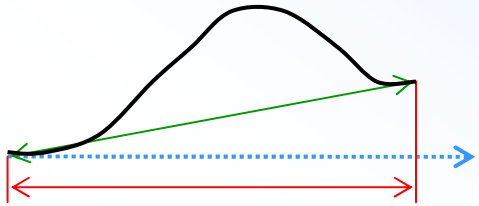
Worm-like chain (Kratky-Porod) semiflexible/stiff polymers

free rotating chain



persistence length, l_p , is an **average** projection of end-to-end distance in the direction of the first bond for n→∞

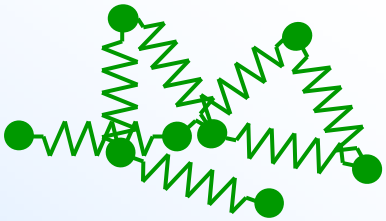
worm-like chain $l\rightarrow 0$ and $\theta \rightarrow 0$ l_p=const

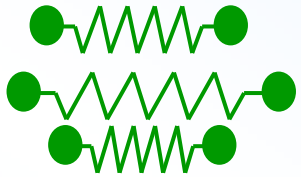


$l_p= b/2$

Bead-spring model – Gaussian chain

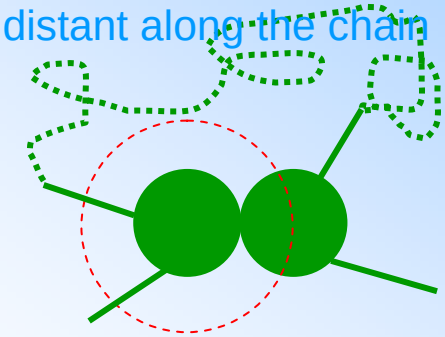
the distance between beads i and j $(i - j >>0)$ in a freely-jointed chain has a Gaussian distribution
in a Gaussian chain it holds for any I, j
a physical realization is a bead-spring model





Real chains

long-range interactions - excluded volume *v*
expand macromolecule
but elasticity resists

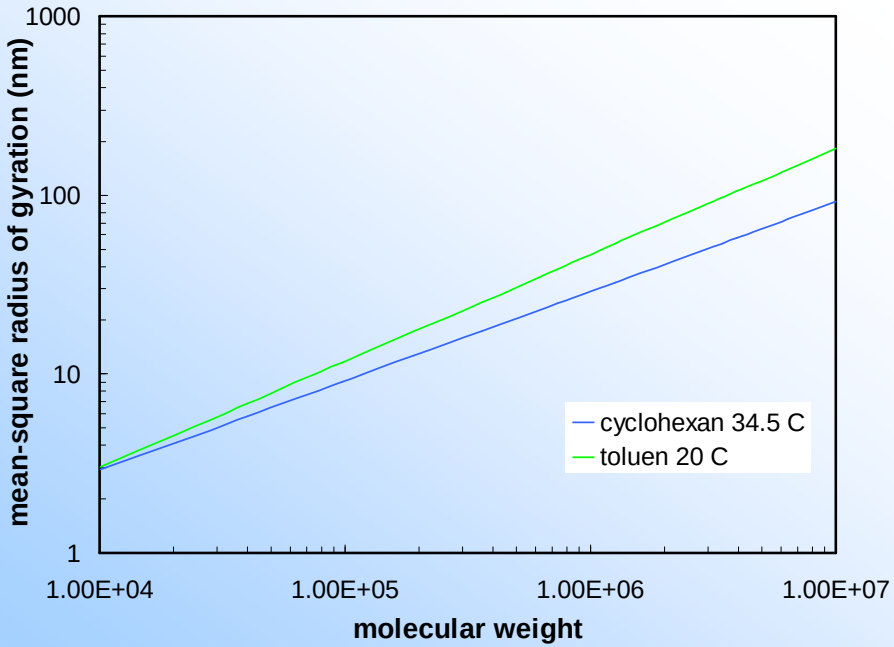


hard spheres
entropic
athermal solvent

total excluded volume ~ N^2

$$\frac{A}{kT} \cong \frac{R^2}{Nb^2} + b^3 \frac{N^2}{R^3} \qquad \frac{dA}{dR} = 0 \quad \Rightarrow \quad R \approx N^{0.6}$$

in reality also *U*; *v* can be <*0*
bad, theta and good solvents

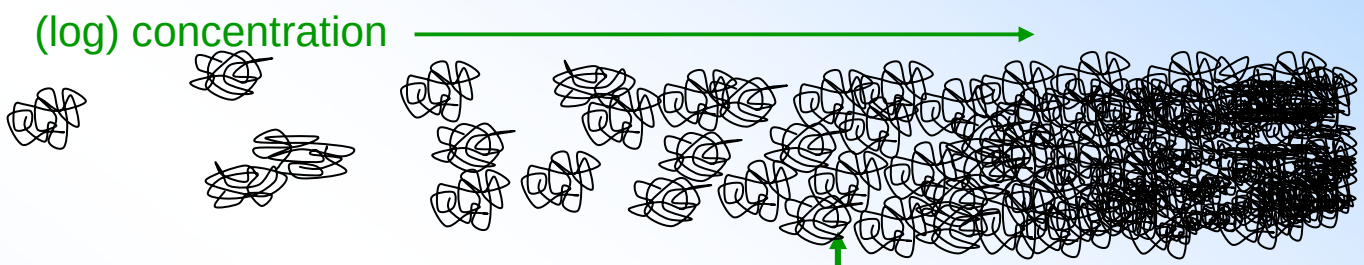


Two parameter theory of dilute polymer solutions

unperturbed dimensions
excluded volume

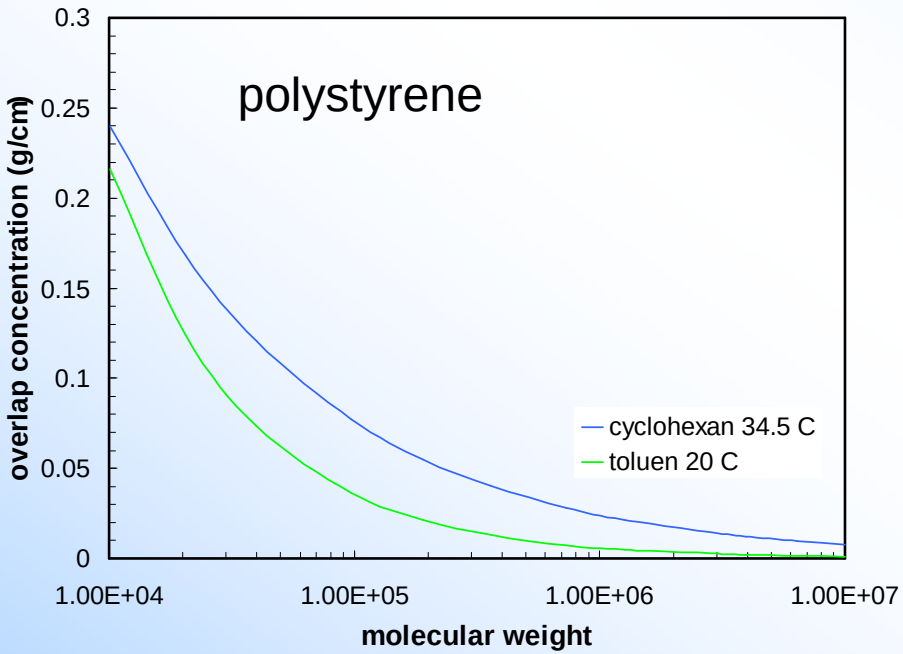
Intramolecular excluded volume ⇒ isolated macromolecules ⇒ infinite dilution

Concentration regimes in polymer solutions



c* overlap concentration – $c_c=c_T$

$$c^* \approx \frac{M}{R_g^{\,3}}$$



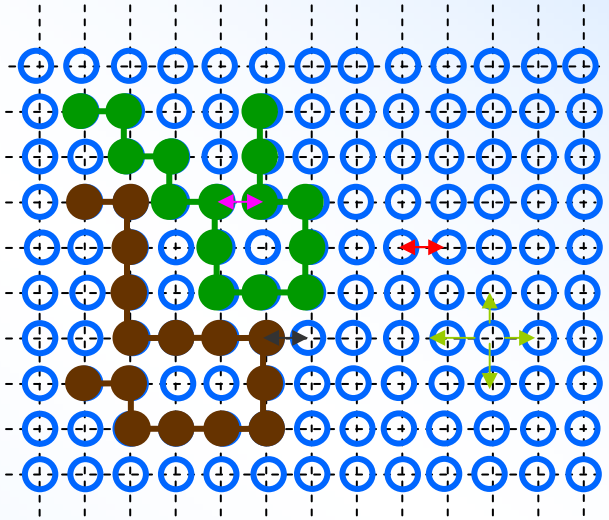
Thermodynamics

model of polymer solution ⇒ free energy of mixing ⇒ equilibrium state of the solution

Flory-Huggins equation
lattice model

$$n = n_s + n_p N \qquad N = \frac{\tilde{v}_p}{\tilde{v}_s}$$

$$\phi = \frac{N n_p}{n}$$



$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S = k(\ln \Omega_{PS} - \ln \Omega_P)$$

$$\frac{-\Delta S}{kn} = \frac{\phi}{N}\ln\phi + (1-\phi)\ln\phi$$

$$\chi = Z(\varepsilon_{ps} - (\varepsilon_{pp} + \varepsilon_{ss})/2)/kT$$

$$\frac{\Delta H}{kT} = \chi\phi(1-\phi)$$

Mean-field theory
local contact probabilities approximated by overall ones

F-H eq. becomes semiempirical as χ has entropic component $\chi = a + \frac{b}{T} + ..$

F-H eq. can be derived for mixing of polymers – polymer blends

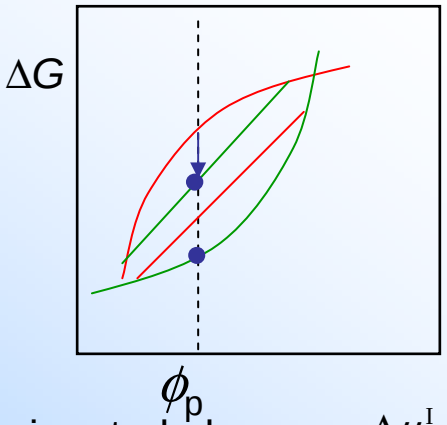
Phase behavior

Solubility parameters δ_p and δ_s $\chi \approx \frac{\tilde{\nu}}{kT}(\delta_p - \delta_s)^2 > 0$ nonpolar systems $\varepsilon_{ps} = \sqrt{\varepsilon_p \varepsilon_s}$

(missing entropic part)

General criterion of solubility $\Delta G<0$ is met with amorphous polymers even if $\chi>0$

So the question is: Can ΔG decreases on phase separation?



$\frac{\partial^2 \Delta G}{\partial \phi_p^{\,2}}$

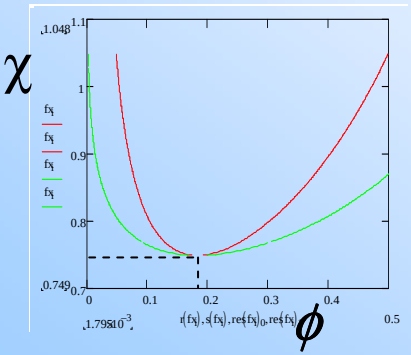
<0 unstable

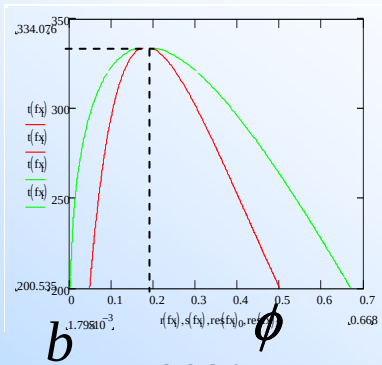
=0 border – spinodal line

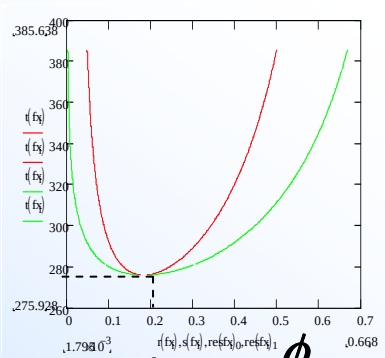
>0 stable

For conjugated phases: $\Delta\mu_x^{I} = \Delta\mu_x^{II}$ $x = s, p$ $\Delta\mu_x = \left(\frac{\partial \Delta G}{\partial n_x}\right)_{T,p,n-n_x}$ coexistence curve – binodal line

N=20







$N \to \infty$

$\chi_{crit} \to 0.5$

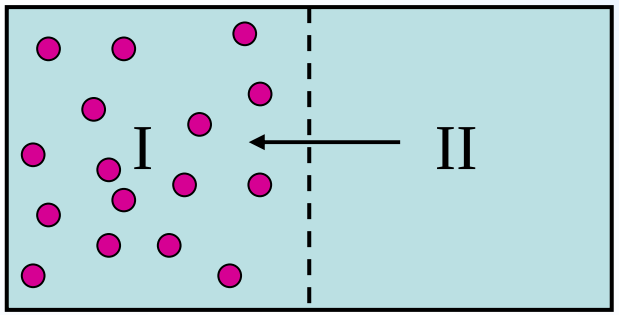
$\phi_{crit} \to 0$

$CST \to \theta$

$\chi = a + \frac{b}{T}$ upper < lower critical solution temperature

Osmosis – osmotic pressure

semipermeabile membrane



$$\mu_s^{I} = \mu_s^{II}$$
$$\mu_s^{I}(p,\phi) < \mu_s^{II}(p,0)$$
$$\mu_s^{I}(p+\Pi,\phi) = \mu_s^{II}(p,0)$$

$$\Pi = \left(\frac{\partial \Delta G}{\partial V}\right)_{np} = \tilde{v}_s RT\left(\frac{\phi}{N} - \ln(1-\phi) - \phi - \chi\phi^2\right)$$

dilute solution

$$\Pi = \tilde{v}_s RT\left(\frac{\phi}{N} + (\tfrac{1}{2} - \chi)\phi^2 + \tfrac{1}{3}\phi^3 + ...\right)$$

$$\Pi = RT\left(\frac{c}{M} + A_2 c^2 + A_3 c^3 + ...\right)$$

$T = \theta \Rightarrow A_2 = 0$

0<<c $\Rightarrow$ exl. vol $\rightarrow$0

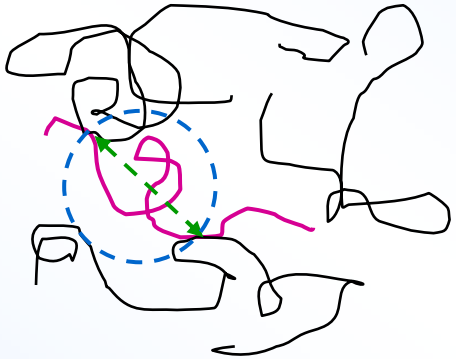
semidilute solutions ($\phi^* < \phi << 1$)

$$\frac{\Pi}{RT} \cong C_{\text{blob}} \sim c^{9/4}$$

$$\sim c_\theta^{\ 3}$$

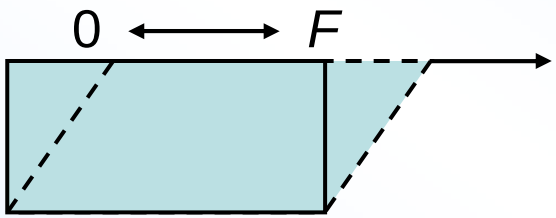
blob ξ^3

correlation length ξ



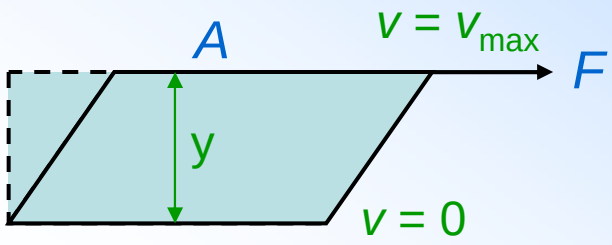
Flow, rheology, molecular hydrodynamics

elastic body



shear

viscous body



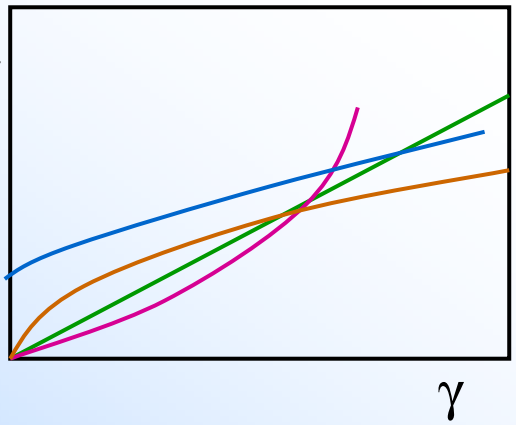
$$\tau = \frac{F}{A} = \eta \frac{\mathrm{d}v}{\mathrm{d}y} = \eta\dot{\gamma}$$

shear stress=viscosity x shear rate

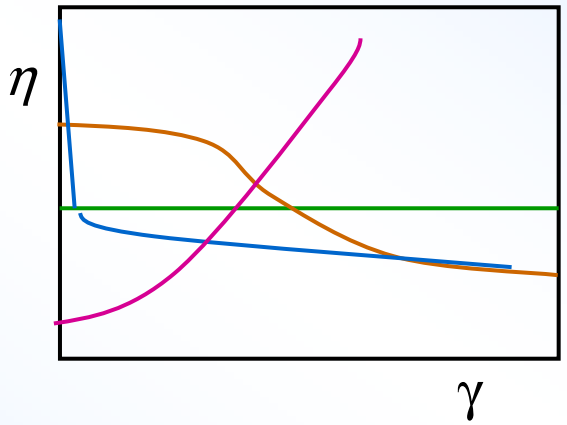
Newto nian liquid

$$\eta(\dot{\gamma}) = \text{const}$$

flow curves



viscosity curves



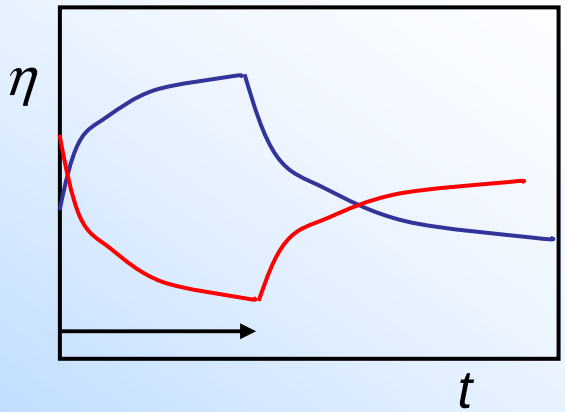
shear thickening (dilatancy)

shear thinning

pseudoplasticity

time dependence

$$\dot{\gamma} = \text{const}$$



thixotrophy structure breaking
associative polymers

rheopexy
(negative thixotrophy)
structure forming
ionomers in nonpolar solvent

Viscosity of solution η=η(ϕ) for dilute solution $\eta(\phi) = \eta_0(1 + a_1\phi + a_2\phi^2 + \ldots)$

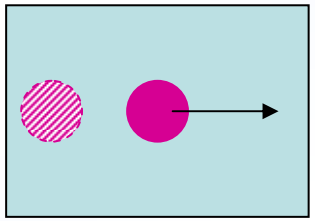
Hard spheres Einstein a_1=2.5 ϕ usually used for dispersions. Polymers: mass concentration.

$\eta(c) = \eta_0(1 + [\eta]c + k_H[\eta]^2 c^2 + \ldots)$ [η] intrinsic viscosity (cm³/g); k_H Huggins constant

$$[\eta] = \frac{10 N_A \pi R^3}{3M}$$

reciprocal particle density

friction coefficient



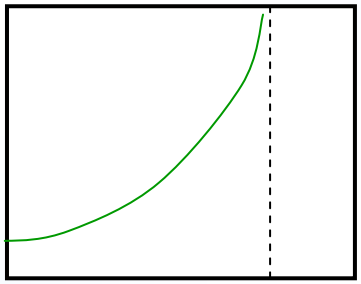
$F = fv$

hard sphere Stokes law

$f = 6\pi\eta_0 R$

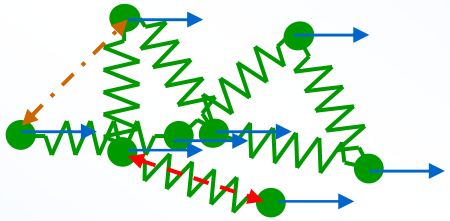
Empirical equation for viscosity a suspension of hard spheres Mooney equation

$$\frac{\eta}{\eta_0} = \exp\left(\frac{2.5\phi}{1 - \frac{\phi}{\phi_c}}\right)$$

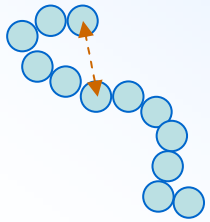


ϕ_c (maximum packing fraction)

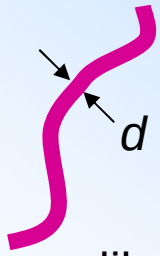
models used for polymer (hydro)dynamics



bead-spring
Rouse (free-draining)
Zimm (&hydrodynamic interactions)



pearl-necklace
Kirkwood-Riseman



wormlike
(semiflexible)

finite dimensions (Stokes law)

friction coefficient
total resistance

intrinsic viscosity
additional stress

flexible polymers in theta solvent

$$[\eta]_\theta = \Phi_0 \frac{\left\langle R^2 \right\rangle_0^{3/2}}{M} \Rightarrow [\eta]_\theta \sim M^{1/2} \qquad \frac{f_\theta}{\eta_0} = [f]_\theta = \mathrm{P}_0 \left\langle R^2 \right\rangle_0^{1/2} \Rightarrow [f]_\theta \sim M^{1/2}$$

$\Phi_0 = 2.2 - 2.9\,10^{23}\ \mathrm{mol}^{-1}$ $\quad \mathrm{P}_0 = 5.2 - 6.0$ hydrodynamic radii of HES $R_f < R_\eta$

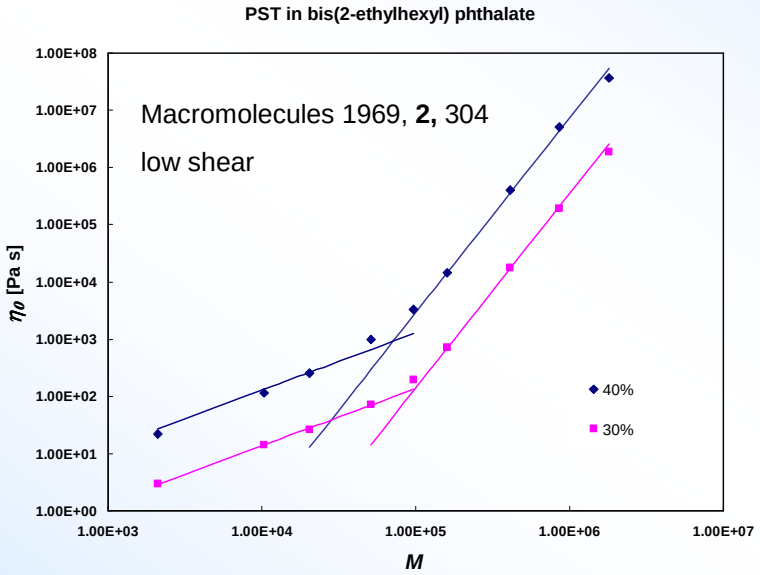
good solvents – Flory Fox theory: one expansion factor $\alpha_R = \alpha_\eta = \alpha_f$

$$[\eta] = [\eta]_\theta \alpha_\eta^{\ 3} = \Phi_0 \frac{\left\langle R^2 \right\rangle^{3/2}}{M} \Rightarrow [\eta] \sim M^{0.8} \qquad [f] = [f]_\theta \alpha_f = \mathrm{P}_0 \left\langle R^2 \right\rangle^{1/2} \Rightarrow f \sim M^{0.6}$$

Strictly speaking, $\alpha_R \neq \alpha_\eta \neq \alpha_f$

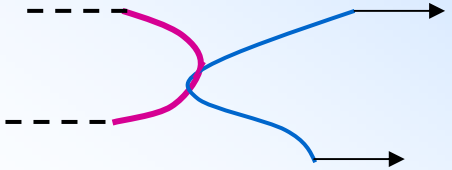
Empirical Mark-Houwink Eq. $[\eta] = KM^a$
a=0.5 (theta) to 0.8 (athermal) < (rigid)

semidilute/ concentrated solutions, polymer melts



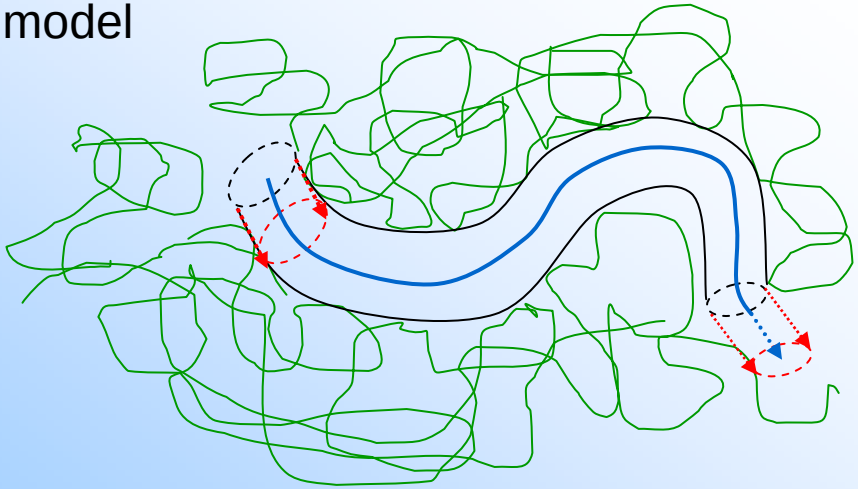
$\eta \sim M$ for short-chain polymers
well described by Rouse model
hydrodynamic interaction is shielded

Steeper increase $\eta \sim M^{3.4}$ above certain M_c
chain entaglement



entanglement of polymer chains= temporal crosslinking $\Rightarrow$ viscoelasticity

reptation model



while the chain sneaks through the polymer, the confining **tube** disappears and renews

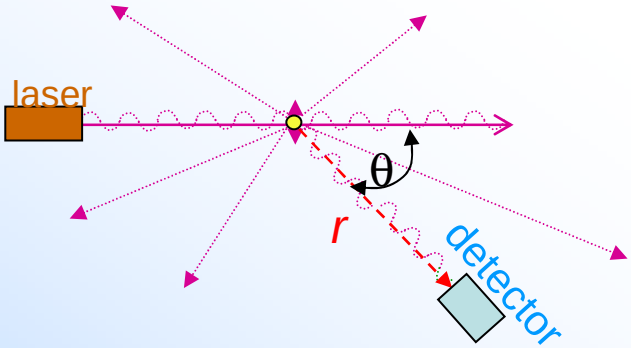
$\eta \sim M^3$

Light Scattering by Macromolecular Solution

Static Light Scattering by macromolecular solutions

elastic scattering by independent small particles
Raleigh scattering (L<λ/20; general solution of Maxwell eqs.→ Mie)

oscillating induced dipole



$$\frac{I_s}{I_0} = \frac{16\pi^4\alpha^2}{\lambda^4 r^2}\frac{cM}{N_A} = \frac{4\pi^2 n^2}{\lambda^4 r^2}\left(\frac{dn}{dc}\right)^2\frac{cM}{N_A}$$

$$R_\theta = \frac{I_s r^2}{I_0} = \frac{4\pi^2 n^2}{\lambda^4}\left(\frac{dn}{dc}\right)^2\frac{cM}{N_A} = KcM$$

dn/dc refractive index increment

R_θ Raleigh ratio

K optical constant

vertically polarized light
observed in the horizontal plane

$I_s \sim \lambda^{-4} \Rightarrow$ blue sky/red sunset

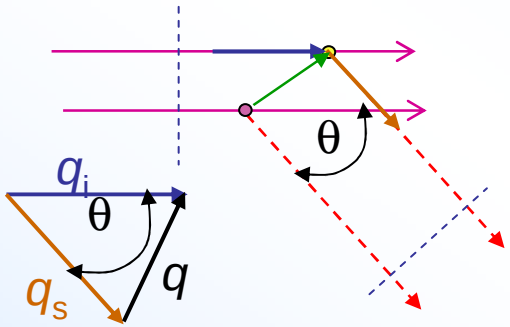
scattering by solution

destructive interference in regular structures (crystals, polyelectrolytes)
fluctuation in polarizability ~ fluctuation in concentration ⇐ free energy

$$\frac{Kc}{R_\theta} = \frac{1}{RT}\left(\frac{\partial\Pi}{\partial c}\right)_T = \frac{1}{M} + 2A_2c + \ldots.$$

scattering by larger particles

phase difference

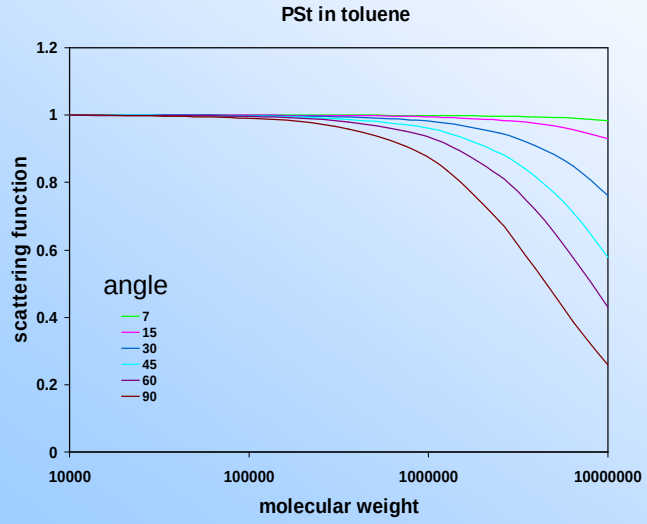


position vector
incident wavevector $\mathbf{q_i}$
scattered wavevector $\mathbf{q_s}$
scattering wavevector $\mathbf{q}$

$$\vec{q} = \vec{q}_i - \vec{q}_s \qquad |\vec{q}_i| = |\vec{q}_s| = \frac{2\pi n}{\lambda} \qquad |q| = \frac{4\pi n}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

Angular scattering function

$$S(q) = \frac{I_s(\theta)}{I_s(0)} = \left\langle \left| \frac{1}{P^2}\sum_{j=1}^{P} \exp(i\vec{q}\vec{r}_j) \right| \right\rangle = \frac{1}{P^2}\sum_{i=1}^{P}\sum_{j=1}^{P}\frac{\sin(qr_{ij})}{qr_{ij}} = \frac{1}{P^2}\sum_{i=1}^{P}\sum_{j=1}^{P}\left(1 - \frac{q^2 r_{ij}^2}{3!} + ...\right) = 1 - \frac{16\pi^2 n^2}{3\lambda^2} R_g{}^2 \sin^2\left(\frac{\theta}{2}\right) + ...$$



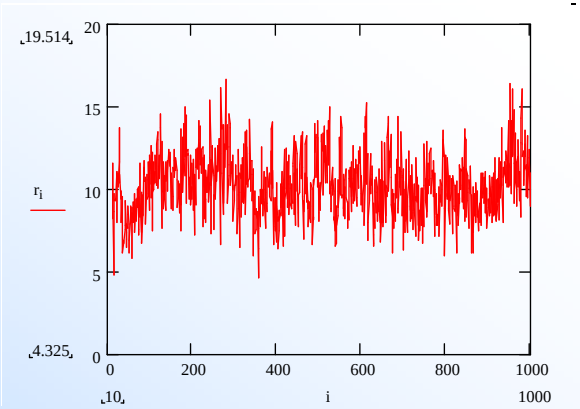
SLS → M, A_2, R_g

Principles apply also to other types of radiation – neutrons, x-ray (different λ; different scatterers)

Dynamic (Quasi-Elastic) Light Scattering

macroscopically homogeneous system (liquid) scatters light due to polarizability fluctuations

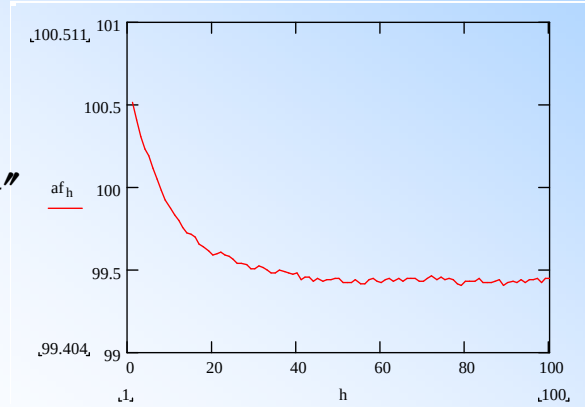
consequently the instantaneous intensity of scattered light fluctuates



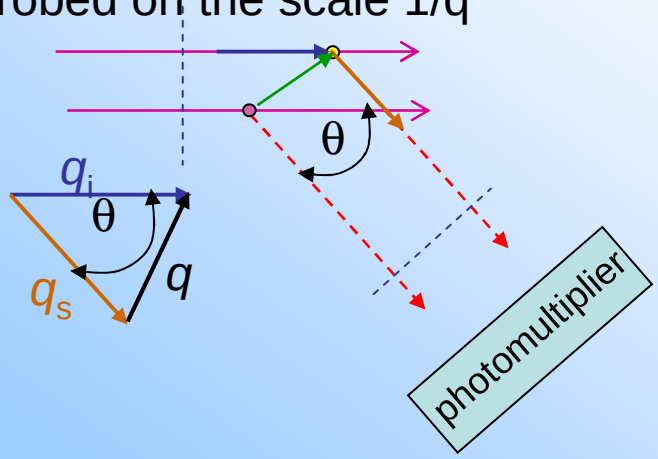
I_s values seems random but they are correlated as fluctuations dissipation is governed by hydrodynamics

time autocorrelation function

$$\langle I(0)I(t)\rangle = \lim_{t'\to\infty}\frac{1}{t'}\int_0^{t'} I(t'')I(t''+t)dt''$$



In DLS fluctuations in concentration are probed on the scale 1/q



Memory of the state is lost when all molecules leave volume element q^{-3} thus the correlation time is given by q and D (diffusion coefficient)

$$\langle I(q,0)I(q,t)\rangle = B + \left(A\exp(-q^2Dt)\right)^2$$

$$D = \frac{kT}{f}$$ Einstein relation

Literature:

M. Rubinstein and R.H. Colby, *Polymer physics* Oxford University Press Inc.,New York, 2003

I. Teraoka, *Polymer Solutions: An Introduction to Physical Properties* Wiley, New York 2002

www.iupac.org/publications/books/pbook/PurpleBook-C3.pdf

UNESCO/IUPAC Postgraduate Course in Polymer Science

Polymer solutions in a nutshell

- Institute of Macromolecular Chemistry ASCR, Heyrovsky sq. 2, Prague -162 06
- http://www.imc.cas.cz/unesco/index.html
- unesco.course@imc.cas.cz