Структура полимеров и композитов

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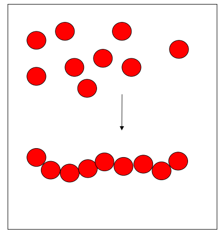
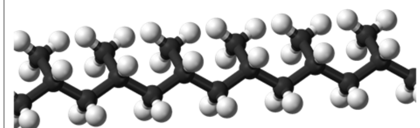
What is a polymer?

- A long molecule made up from lots of small molecules called ***monomers***.





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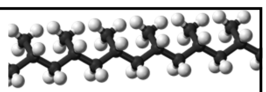
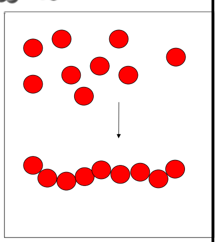
What is a polymer?



- typical energy scales:
  - *C-C bond 350 kJ/mol (=3.5 eV)* [1]
    - *At room temperature k_BT = 2.5 kJ/mol (=25 meV)*
  - *intermolecular interactions*
    - *Hydrogen bond*
    - *dipole-dipole*
    - *van der Waals*
    - *10-100 times weaker than covalent bonding*



[1]J. E. Huheey, E. A. Keiter, and R. L. Keiter, Inorganic Chemistry, 4th ed. (1993)

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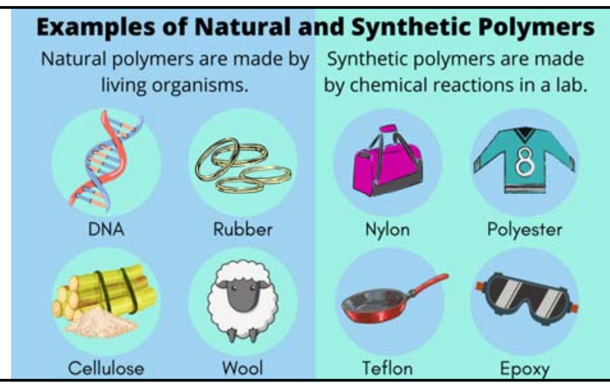

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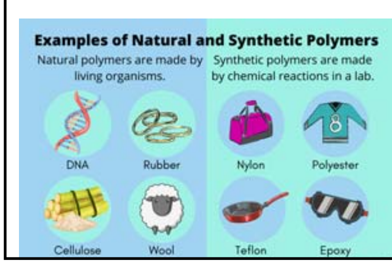
Can you think of an application where polymers are not used?

I failed to find one…



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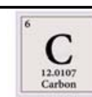
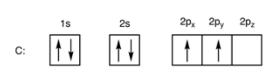
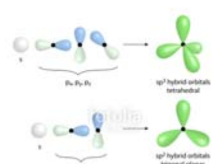
Carbon



- Element #6
  - → 6 electrons
- 1s2 2s2 2p2
- sp^2 hybridization: trigonal planar
  - example: graphene
  - bond angle 120°
- sp^3 hybridization: tetrahedral 3D
  - examples: diamond, methane CH_4
  - bond angle 109.5°





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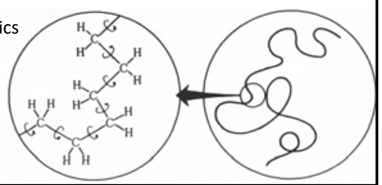
Example: Polyethene (=Polyethylene)

- in an ideal solvent
- undergoing random conformations
- bond angle 109.5°

- described by statistical mechanics
- entropy is very important



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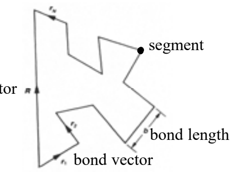
Polymer conformations



End – to – end vector $\vec{R} = \sum_{i=1}^{N} \vec{r}_i$

Average $\langle \vec{R} \rangle = 0$

$$\langle \vec{R}^2 \rangle = \langle \vec{R} \cdot \vec{R} \rangle = \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \vec{r}_i \cdot \vec{r}_j \right\rangle = \sum_{i=1}^{N} \langle \vec{r}_i^{\,2} \rangle + \left\langle \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} \vec{r}_i \cdot \vec{r}_j \right\rangle$$

→ 0 for large |j−i|

$= Nb^2$ $\quad \propto N$

$$\langle \vec{R}^2 \rangle \propto N \quad \Rightarrow \quad \sqrt{\langle \vec{R}^2 \rangle} \propto N^{1/2}$$

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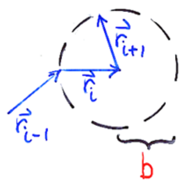
Chain models: freely jointed chain

$$\langle \vec{R}^2 \rangle = \sum_{i=1}^{N} \langle \vec{r}_i^{\,2} \rangle + \left\langle \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} \vec{r}_i \cdot \vec{r}_j \right\rangle$$

$$\langle \vec{r}_i \cdot \vec{r}_j \rangle = \begin{cases} b^2, & i = j \\ 0, & i \neq j \end{cases}$$

$$\langle \vec{R}^2 \rangle = \sum_{i=1}^{N} \langle \vec{r}_i^{\,2} \rangle + \left\langle \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} \vec{r}_i \cdot \vec{r}_j \right\rangle = Nb^2$$



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Chain models: fixed bond angle

$$\langle \vec{r}_i \cdot \vec{r}_i \rangle = b^2$$

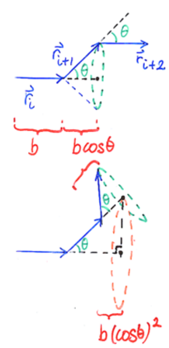
$$\langle \vec{r}_i \cdot \vec{r}_{i+1} \rangle = b^2 \, (\cos\theta)^1$$

$$\langle \vec{r}_i \cdot \vec{r}_{i+2} \rangle = b^2 \, (\cos\theta)^2$$

...

$$\langle \vec{r}_i \cdot \vec{r}_j \rangle = b^2 \, (\cos\theta)^{|j-i|}$$

For sp^3 hybridization: $\cos(180° - 109.5°) = 1/3$



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Chain models: fixed bond angle

$$\langle \vec{R}^2 \rangle = \sum_{i=1}^{N} \langle \vec{r}_i^{\,2} \rangle + \left\langle \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} \vec{r}_i \cdot \vec{r}_j \right\rangle \qquad \langle \vec{r}_i \cdot \vec{r}_j \rangle = b^2 \, (\cos\theta)^{|j-i|}$$

$$\langle \vec{R}^2 \rangle = \sum_{i=1}^{N} b^2 [1 + 2(\cos\theta)^1 + 2(\cos\theta)^2 + 2(\cos\theta)^3 + \cdots] +$$

$$\langle \vec{R}^2 \rangle = Nb^2 + 2Nb^2[(\cos\theta)^1 + (\cos\theta)^2 + (\cos\theta)^3 + \cdots]$$

$$\langle \vec{R}^2 \rangle = Nb^2 \left[1 + 2\frac{\cos\theta}{1-\cos\theta}\right] = Nb^2 \frac{1+\cos\theta}{1-\cos\theta}$$

$$\langle \vec{R}^2 \rangle = Nb_{\text{eff}}^2 \text{ with } b_{\text{eff}} = b\sqrt{\frac{1+\cos\theta}{1-\cos\theta}}$$

For sp^3 hybridization: $b_{\text{eff}} = b\sqrt{2}$

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Diffusion analogy

Cf. one diffusing colloidal particle or molecule (Einstein):

$$\langle \vec{R}^2 \rangle = 6Dt$$

($6D \leftrightarrow b^2$, $t \leftrightarrow N$)

An (ideal) polymer is like the **trajectory** of a diffusing particle!

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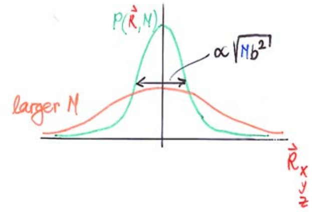
End-to-end distance distribution

$$P(\vec{R},N)=\left(\frac{3}{2\pi Nb^2}\right)^{3/2}\exp\left(-\frac{3\vec{R}^2}{2Nb^2}\right)$$



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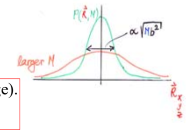
Central Limit Theorem



Consider the sum of N independent, stochastic variables (N is large).
This sum has a normal (= Gaussian) distribution with $\sigma^2 \propto N$.

$$\vec{R}=\sum_{i=1}^{N}\vec{r}_i \;\Rightarrow\; \sigma_{\vec{R}}^2=\left\langle\left(\vec{R}-0\right)^2\right\rangle=\left\langle\vec{R}^2\right\rangle\propto N\left(\times b_{eff}^2\right)$$

Variation in $\vec{R}^2$: $\sigma_{\vec{R}^2}=\sqrt{\left\langle\left(\vec{R}^2-\left\langle\vec{R}^2\right\rangle\right)^2\right\rangle}=\sqrt{\frac{2}{3}}Nb^2$

A Gaussian coil is a *strongly fluctuating object*!

Conclusion: many (global) properties of polymers do not depend on the (local) details of the model.

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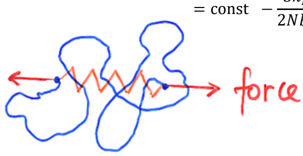
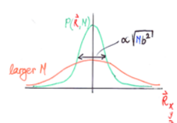
Entropy of a Gaussian coil

$$S(\vec{R}) = k_B \ln W$$
$$= \text{const} + k_B \ln P(\vec{R})$$
$$= \text{const} - \frac{3k_B}{2Nb^2}\vec{R}^2$$





$$P(\vec{R},N)=\left(\frac{3}{2\pi Nb^2}\right)^{3/2}\exp\left(-\frac{3\vec{R}^2}{2Nb^2}\right)$$

$A(\vec{R})(=-TS) = \text{const} + \frac{3k_BT}{2Nb^2}\vec{R}^2$ ENTROPIC SPRING

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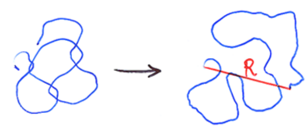
Non-ideal polymer chains

$U[c(\vec{R})]=Nk_BTBc(\vec{R})$

B is the second virial coefficient ($B>0$ repulsion)

Edwards (1965): $\left\langle\vec{R}^2\right\rangle\propto N^{6/5}$



SHORT-RANGE REPULSION: swelling

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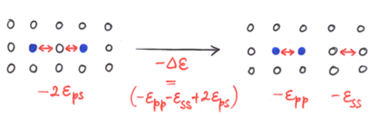
Repulsion combined with attraction

Assumptions:
- only attraction between nearest neighbours
- coordination number: z
- solvent-solvent / solvent-polymer / polymer-polymer

- random **pair** contacts:



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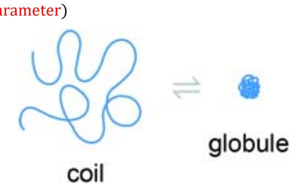
introduction to Flory-Huggins theory

Structure is controlled by the $\frac{z\Delta\varepsilon}{k_BT}\equiv\chi$ (chi−parameter)



- at $\chi=0$ swollen chain $R^*\propto N^{3/5}$
- at $\chi=1/2$ (θ − temperature): ideal chain $R^*=R_0^*\propto N^{1/2}$
- at $\chi>1/2$: collapsed globule, $R^*=R_0^*\propto N^{1/3}$
  the transition is rather sharp for large N

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Going to concentrated solutions and polymeric solids

- there are multiple models
- too short time to discuss them here
- only a few concepts are discussed below

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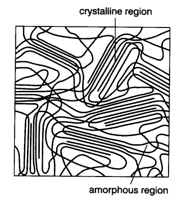
Semi-crystalline polymers

- Areas in polymer where chains packed in regular way.
- Both amorphous and crystalline areas in same polymer.
- Crystalline - regular chain structure - no bulky side groups.
- More crystalline polymer - stronger and less flexible.



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Chain length effect

- Critical length needed before strength increases.
- Hydrocarbon polymers average of 100 repeating units necessary but only 40 for nylons.
- Tensile strength measures the forces needed to snap a polymer.
- More tangles + more touching!!!

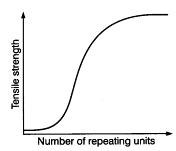

Figure 31 The relationship between tensile strength and chain length for a polymer.

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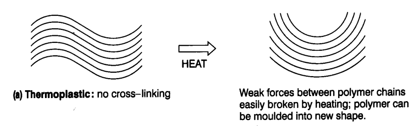
Thermoplastics (80%)



- No cross links between chains.
- Weak attractive forces between chains broken by warming.
- Change shape - can be remoulded.
- Weak forces reform in new shape when cold.

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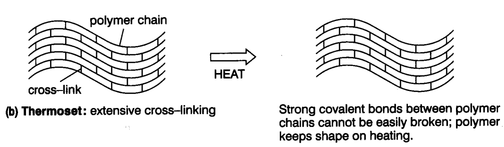
Thermosets



- Extensive cross-linking formed by covalent bonds.
- Bonds prevent chains moving relative to each other.

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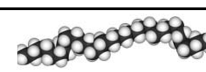
Homopolymers



- All monomers are of the same type
  A + A + A + A + A + … → -A-A-A-A-A-
- Examples:
  - polyethylene
  - Polyvinyl chloride (PVC)

Monomer type affects the intermolecular interactions but also…

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Polymer properties affected by

- chain length,
- presence and type of side groups,
- chain branching,
- stereoregularity,
- chain flexibility,
- crystallinity,
- cross linking…

- and this is not yet all!

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Homo- and hetero-polymers

1. homopolymer
2. alternating copolymer
3. random copolymer
4. block copolymer
5. grafted copolymer

Mankash, Wikipedia commons

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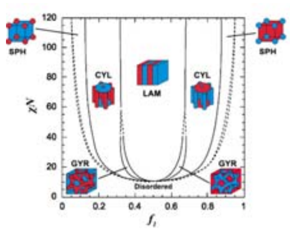
Self-assembled structures of block co-polymers

- Appear for sufficiently high asymmetry parameter.

- Tunable structure.



A.H. Hofman, PhD thesis, RUG, 2016

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Composite materials

- consist of two or more constituent materials
  - e.g., reinforced concrete
  - plywood
  - fiber-reinforced plastics
  - …

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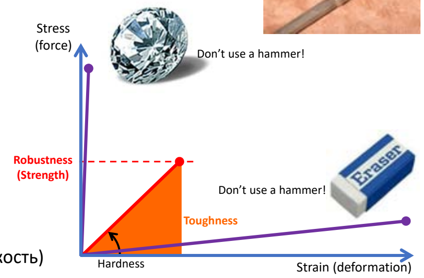
Hardness, robustness & toughness



- Hardness (Твердость)
- Robustness (Прочность)
- Toughness (Ударная вязкость)

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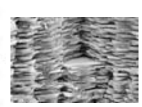
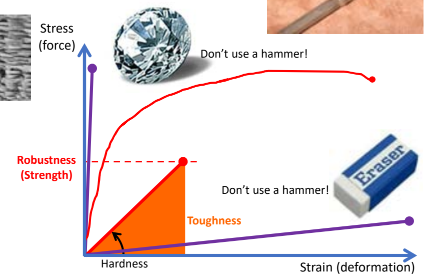
Hardness, robustness & toughness





- Composite materials
  - E.g., Bones
  - Nacre (перламутр)

- Soft matter is usually not hard but composites can be strong and tough!

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Composite materials

- E.g., carbon nanofibers
  - sp^2 chemical bonds in graphite are stronger than in diamond
    - however, weak interlayer bonding
  - use nanofibers to reinforce polymers!

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Structural studies with x-rays

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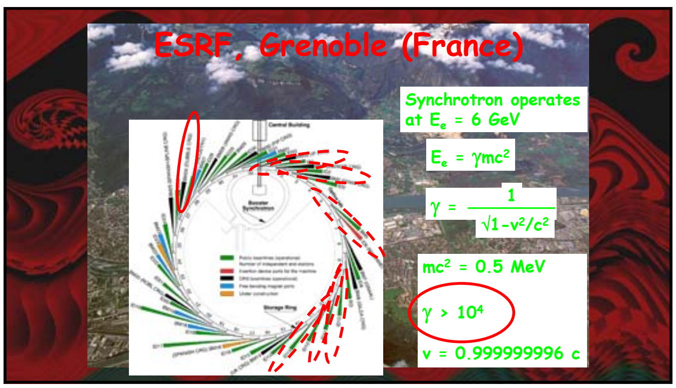

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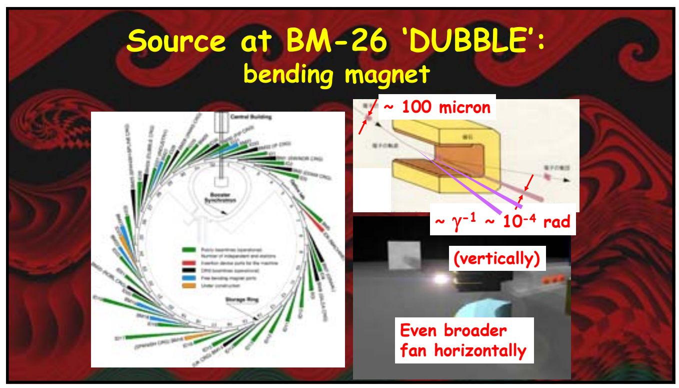

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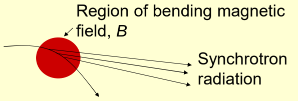
Synchrotron radiation: undulators



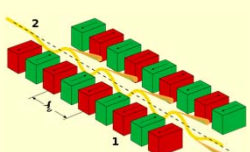
Electron beam of energy E

Characteristic energy, E_c

$$E_c = 0.665BE^2 \text{ keV}$$

E is in GeV , B is in T

$$\lambda_c = 18.6/BE^2 \text{Angstrom}$$



Undulator

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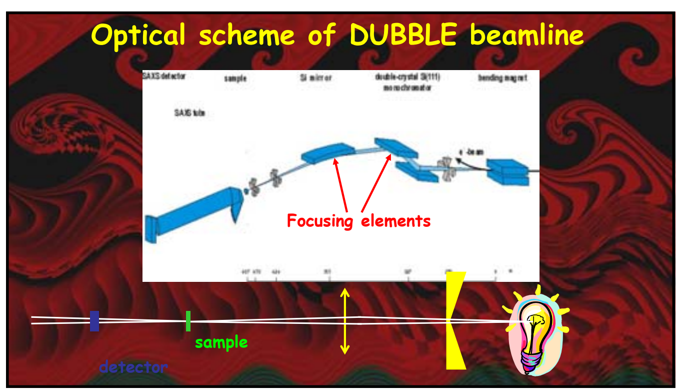

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SynchrotronLIKE in Kaliningrad

- Small angular source size seen from the sample position
- Similar to that at 'large' synchrotron but lower brightness
- Perfect if no time resolution is needed

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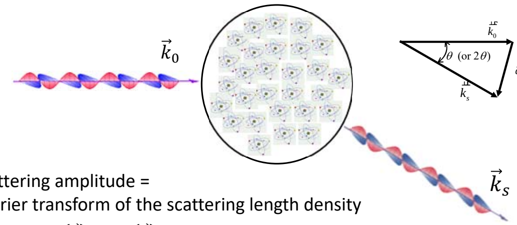
Scattering primer

$$A_s \propto \frac{A_0}{R}\int \zeta(\vec{r})e^{i\vec{q}\cdot\vec{r}}dV$$



- Scattering amplitude = Fourier transform of the scattering length density
- For x-rays $\zeta(\vec{r}) \propto \rho_e(\vec{r})$ to a good approximation
- One measures intensities – phases are missing

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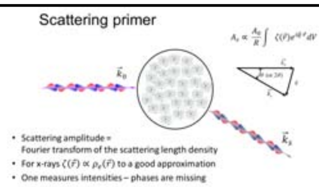
What do we measure?



$$I \propto |A_s|^2 = A_s \times A_s^* = \int \rho_e(\vec{r})e^{i\vec{q}\cdot\vec{r}}d^3\vec{r}\int \rho_e(\vec{r}')e^{-i\vec{q}\cdot\vec{r}'}d^3\vec{r}'$$

replace $\vec{r}' = \vec{r} + \delta\vec{r}$

$$= \iint \underbrace{\rho_e(\vec{r})\rho_e(\vec{r}+\delta\vec{r})\, d^3\vec{r}}_{\text{Density correlation function}}\, e^{-i\vec{q}\cdot\delta\vec{r}}d^3\delta\vec{r}'$$

→ Scattering measures density correlations

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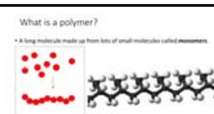
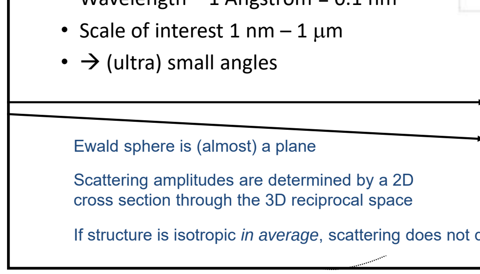
Small-angle approximation

- Wavelength ~ 1 Angstrom = 0.1 nm
- Scale of interest 1 nm – 1 µm
- → (ultra) small angles





Ewald sphere is (almost) a plane

Scattering amplitudes are determined by a 2D cross section through the 3D reciprocal space

If structure is isotropic *in average*, scattering does not depend on the direction

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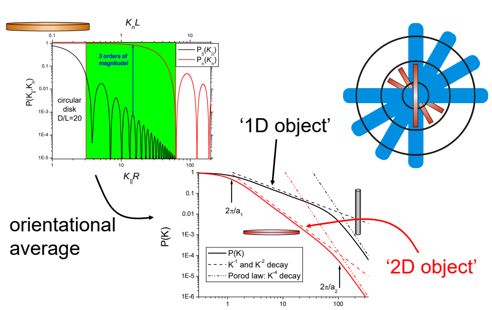
Low-dimensional objects: disks & rods



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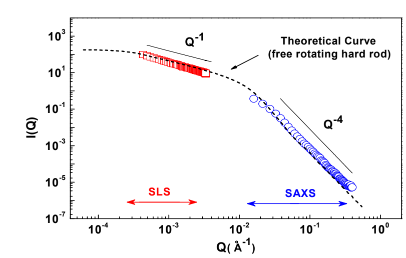
Sepiolite rods



Theory: L = 900 nm (40% polydisperse) and D = 30 nm

ZX Zhang, J. van Duijneveldt (Bristol)

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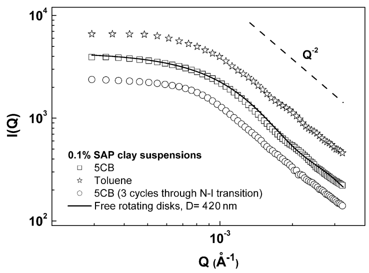
Montmorillonite clay platelets – light scattering



ZX Zhang, J. van Duijneveldt (Bristol)

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Random polymer coils

Polymer in ideal solvent

- mass $M \propto$ contour length L
- $R_g \propto \sqrt{L} \propto \sqrt{M}$, where $R_g = \sqrt{6}\, R_{\text{end-to-end}}$
- $M \propto R_g^2$
- An ideal random coil has the mass dimension of 2
- Looking at scales
  - >> chain diameter
  - << coil size
  - yields $I \propto q^{-2}$ decay

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Random polymer coils: Guinier limit

- Guinier limit:
  - small K
  - scales >> coil size
- Guinier law
  - $I(K) \propto \exp[-(R_g K)^2/3]$
  - $R_g = \sqrt{6}\, R_{\text{end-to-end}}$

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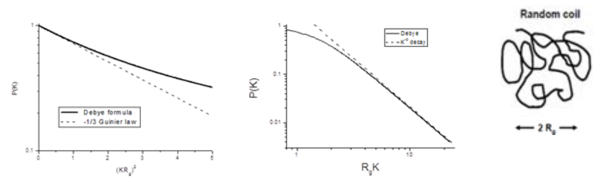
Random polymer coils



$$P(K) = \frac{2}{(R_g K)^4}\left[(R_g K)^2 - 1 + \exp(-(R_g K)^2)\right]$$

$$\exp(-(R_g K)^2) \approx 1 - (R_g K)^2 + \frac{1}{2}(R_g K)^4 - \frac{1}{6}(R_g K)^6 + \cdots$$

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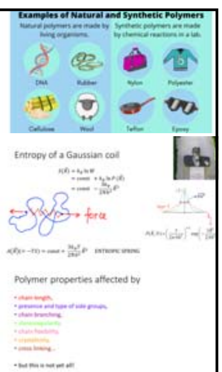
Conclusions

- Polymers are indispensable in modern life
- Strongly influenced by entropy
- Broad opportunities for materials engineering
- More dimensions with composites
- Scattering enlightens the nanostructure



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