Methoden moderner Röntgenphysik I:
Struktur und Dynamik kondensierterMaterie

Vorlesung zum Haupt/Masterstudiengang Physik

WS 2008/9

G. Grübel, M. Martins, E. Weckert et al.

Location:SemRm4, Physik, Jungiusstrasse

Thursdays 10.15 –11.45

G.Grübel (GG), A.Meents (AM), C. Gutt (CG), S. Roth (SR)

Soft Matter Applications

Stephan V. Roth

Introduction   (GG)

Modern Crystallography   (AM)

Coherence based techniques   (CG)

Soft matter applications   (SR)

➡ 22.01.2009   Basics, theory, preparation – a primer

   29.01.2009   Small-angle X-ray scattering and its applications

   03.02.2009   Polymer, colloidal and nanocomposite surfaces

                 (Note change Thursday (5.)-> Tuesday) (3.)

Aim: Overview over use of soft matter and x-ray scattering of soft matter

Aim

Overview over use of soft matter and x-ray scattering of soft matter

Methoden moderner Roentgenphysik I - Vorlesung im Haupt/Masterstudiengang Physik, Universität Hamburg, WS 2008/9 S.V. Roth
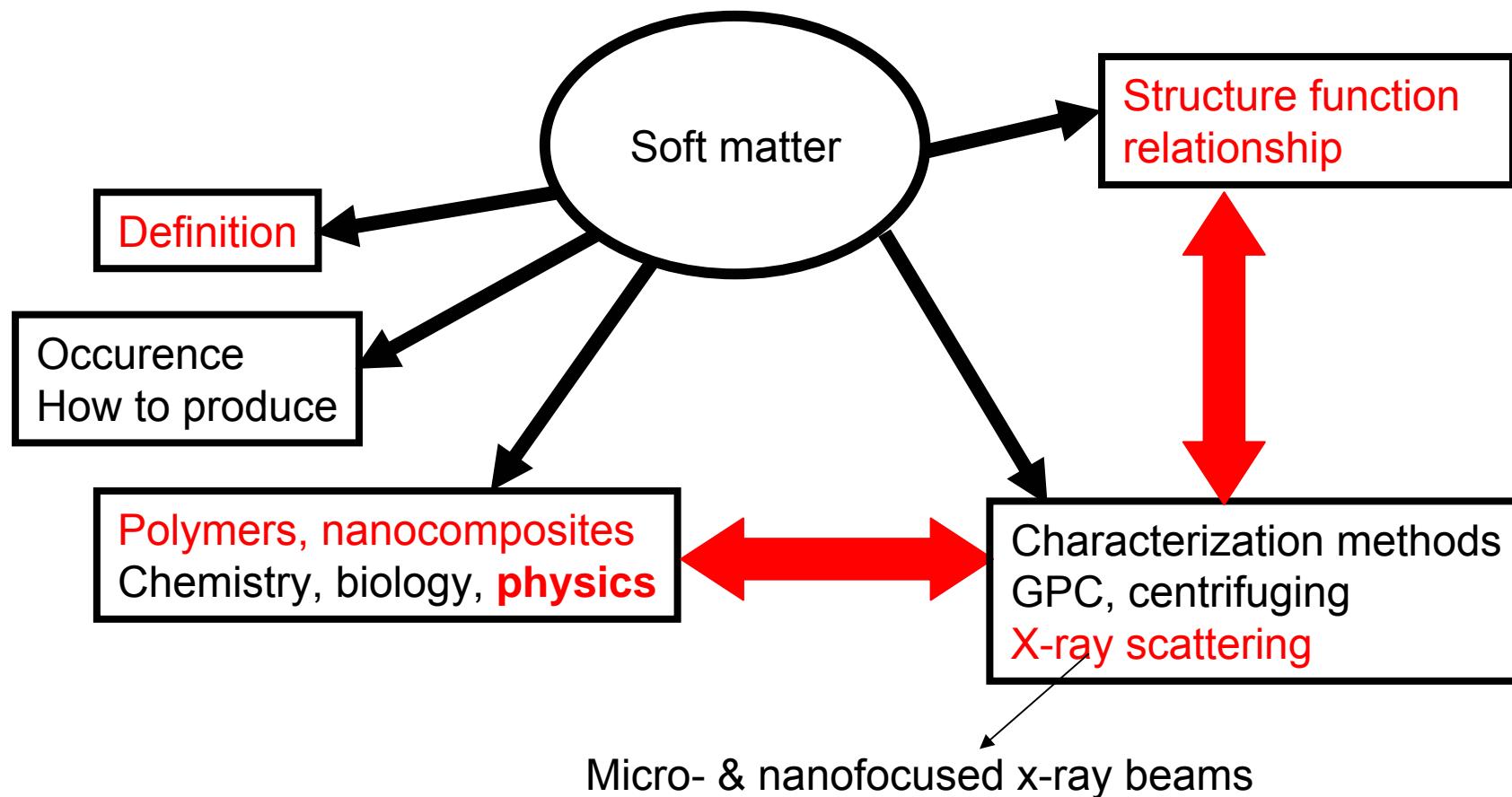
Literature

- [Strobl]   G. Strobl, "The Physics of Polymers", Springerverlag, Heidelberg (1997), ISBN 3-540-63203-4

- [Springer]   T. Springer et al., "Streumethoden zur Untersuchung kondensierter Materie", Forschungszentrum Jülich GmbH, Jülich (1996), ISBN 3-89336-180-4

- [Lechner]   M.D. Lechner et al., "Makromolekulare Chemie", Birkhäuser Verlag, Berlin (1993), ISBN 3-7643-2973-4

- [Lindner]   P. Lindner et al., "Neutron, X-rays and light: Scattering Methods Applied to Soft Condensed Matter", North Holland, Amsterdam (2002), ISBN 0-444-51122-9

- [Stribeck]   N. Stribeck, "X-ray Scattering of Soft matter", Springerverlag, Heidelberg (2007), ISBN 978-3-540-69856-2

- [Higgins]   J.S. Higgins and H.C. Benoit, "Polymers and Neutron Scattering", Clarendon Press, Oxford (1996), ISBN 0 19 850063 7

Basics, theory, preparation – a primer

➢What is soft matter?

➢Basic Definition – a try!

➢Notion for description, constituents, architecture

➢Characterization of polymers, molar masses, polydispersity

➢Chain conformation, constitution, configuration, chain models

➢Flory-Huggins-theory, mixture of polymers, Interaction, phase separation

➢Colloids

➢Polymer-Metal nanocomposites
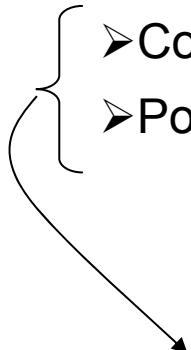
Take care – here, metals (hard matter, actually) comes into play. But it's still soft matter – this is no contradiction, as you will see!

Soft Matter

Soft matter is not hard matter!

Metallic alloys, ceramics…

- ➢ Polymers (bottles)
- ➢ Colloids (wall paintings)
- ➢ Nanocomposites (Metal-Polymer-Composites, airplanes, credit cards)
- ➢ Fibres (Textiles)
- ➢ Wood (natural nanocomposite)
- ➢ Cells (Biology)
- ➢ Glue (quite complex!)
- ➢ …

Focus on specific examples

Characteristics: Polydispersity, heterogeneity
Stribeck: „Scattering, not diffraction"

We will first start with polymers!

Example: Cracks in industrial Polystyrene bulk material

µSAXS

Optical micrograph

same time a high SAXS resolution is ensured which allows for clearly resolving the first order collagen (65 nm) with a maximum resolvable real space structure of 90 nm given by the beamstop size. As the structures of the craze field are on the order of 10 nm - 100 nm (Brown & Kramer, 1981; Salomons et al., 1999b) the SAXS resolution is sufficient to locally investigate the craze field.

2.3. Craze field scanning

The sample was investigated in transmission geometry with the beam parallel to the initial force direction (x), see Fig. 1(a). Two line scans were performed with a step size of $\Delta z = 50 \mu m$ and an overall scan length of 2 mm parallel to the craze in a distance of 400 µm (scan 1) and 500 µm (scan 2) from the craze. Fig. 1(b) shows a photograph of the craze and Fig. 1(c) a photograph of the begin of the area investigated. The first five points of the two line scans are depicted as white circles. The scans both started in the area of the maximum bending amplitude. The scan direction z was chosen along the length of the sample and thus perpendicular to the force applied.
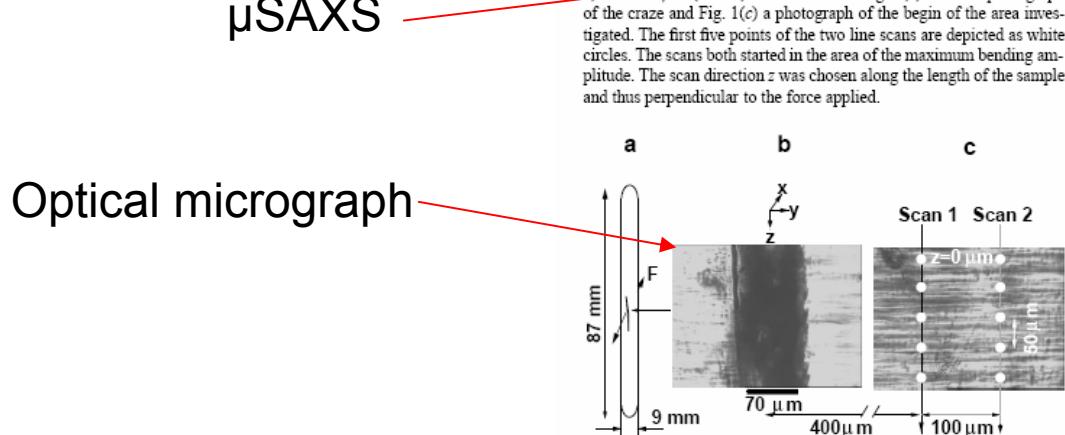
Figure 1
(a) Sample geometry. The thickness in the area investigated was 1 mm. The force F was perpendicular to the sample surface. The crack is indicated as the kinked black line. (b) Photograph of the craze in the area of the maximum bending amplitude. The scale bar is 70 µm. (c) Line scans through the craze field. The beam size was 5 µm (indicated by the white spots), the step size 50 µm. The craze field was measured in transmission geometry with the beam direction parallel to F (x-direction, Fig. 1a).

3. Results

3.1. Data treatment

In Fig. 2 seven representative SAXS patterns are shown. The corresponding scan points are $z = 50 \mu m$, $250 \mu m$, $400 \mu m$, $750 \mu m$, 1000
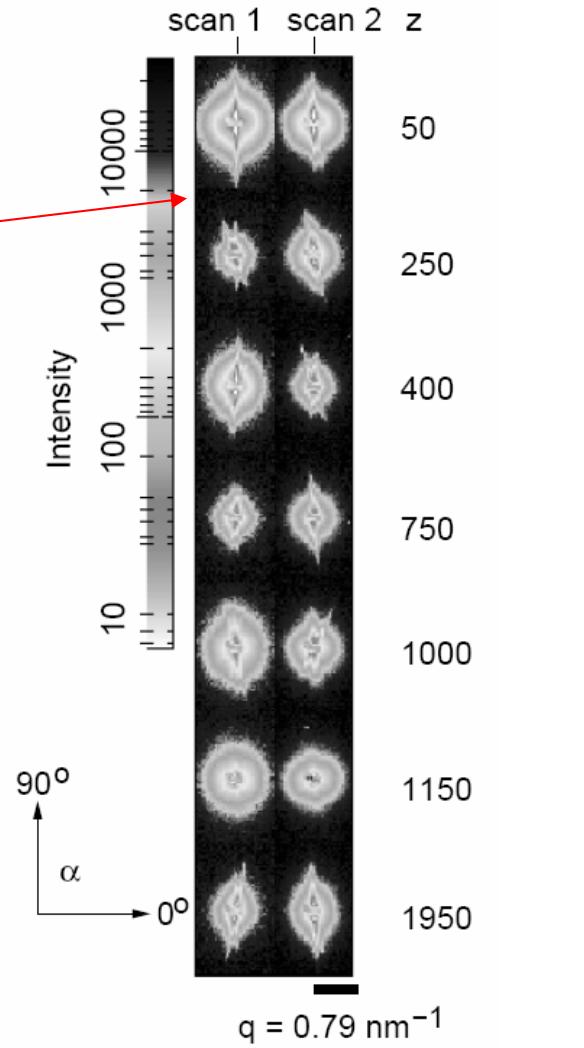
Roth et al., J. Appl. Cryst. 36, 684 (2003)

Strong overlap to materials science

Basic definition

Polymers:
- Macromolecules
- Build up of a large number of molecular units
- Covalent bonds

Molecules: N_2, O_2, H_2, CH_3,…

Standard example: Polyethylene (PE)

Note: Names are often abbreviated by capital letters, e.g.

Polypropylene - PP, Poly(mehtylmethacrylate) – PMMA, Polystryrole (PS),

Poly(ethyelene terephtalate) – PET, Poly(p-phenyleneterephtahalamide) – PPTA: Kevlar

… and often have commonly used trade names: Kevlar, nylon…

Difference in chemical constituents, architecture and hence in physical properties!

Amorphous, crystalline, glassy, viscous,…
Deformation, cracks, SAXS, GISAXS…

Basic definition

Standard example: Polyethylene (PE)

Ethylene:

H   C = C   H
H   H
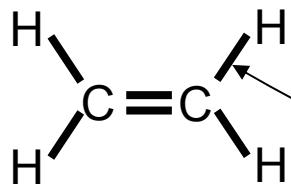
Structure unit
Monomeric unit

Covalent bond:
➢ Interaction between nearest neighbours dominates
➢ Binding and anti-binding orbitals: Spatial overlap of electron wave functions, binding energy
➢ Increased electron density between nuclei
➢ Strongly directed bonding (diamond, sp3-hybridisation)

Polyethylene ... — C — C — C — C — ...

backbone
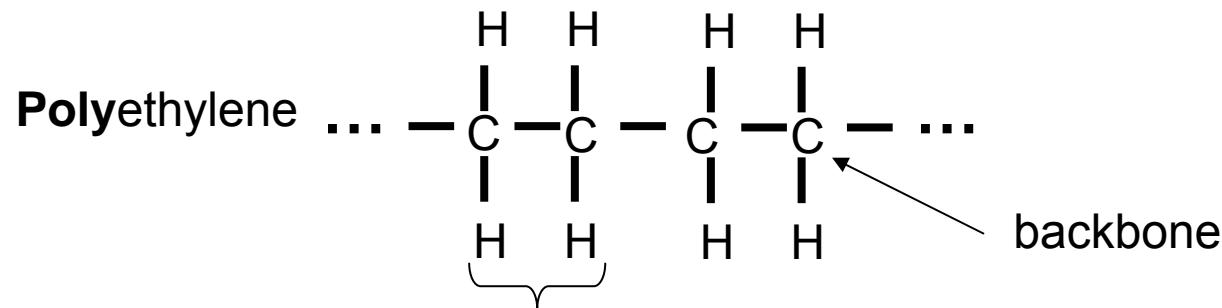
Number of monomers: Degree of polymerization: N
Polymerization process: starts from low molar mass compounds

Distribution functions

Polymerization reactions: mixture of macromolecules of different molecular weight

Monomer: molecular weight M

Distribution function: p(M) -> number density (number per …)
p(M)dM : fraction of polymers M…M+dM

Normalization:
$$\int p(M)dM = 1$$

Number average molecular weight:
$$\overline{M}_n = \int p(M)MdM$$

Strictly speaking: M -> discrete (monomer units), but degree of polymerization high

Weight average:
$$p'(M) = \frac{p(M)M}{\int p(M)MdM} \qquad \overline{M}_W = \int p'(M)MdM = \frac{\int p(M)M \cdot MdM}{\int p(M)MdM}$$

Weight fractions

Distribution functions

$M = P \times M_m$
$M = 5 \times M_m$

$N(M)$

M_m

M

Source: Stribeck

$N(M)$

0.5

0.5

M_n

M

Source: Stribeck

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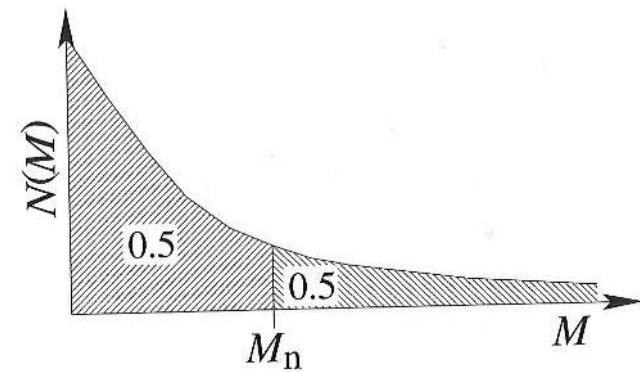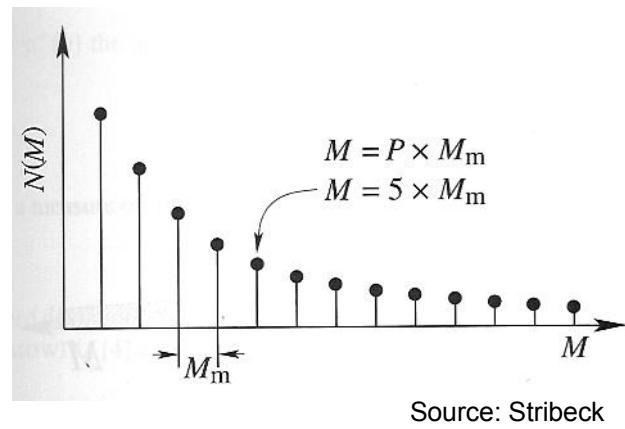
Polydispersity

Note: $\overline{M}_W > \overline{M}_n$ Characterize distribution of molecular weight $U = \dfrac{\overline{M}_W}{\overline{M}_n} - 1$

Variance of p(M) $\left\langle \Delta M^2 \right\rangle = \int p(M)\left(M - \overline{M}_n\right)^2 dM$

$$= \int p(M)M^2 dM - \underbrace{\int p(M)2\overline{M}_n M dM + \int p(M)\overline{M}_n^2 dM}$$

$$= \overline{M}_W \overline{M}_n - \overline{M}_n^2 \ \text{ using } \ \overline{M}_n = \int p(M)M dM$$

$$U = \frac{\overline{M}_W}{\overline{M}_n} - 1 = \frac{\left\langle \Delta M^2 \right\rangle}{\overline{M}_n^2}$$

The polymer chain
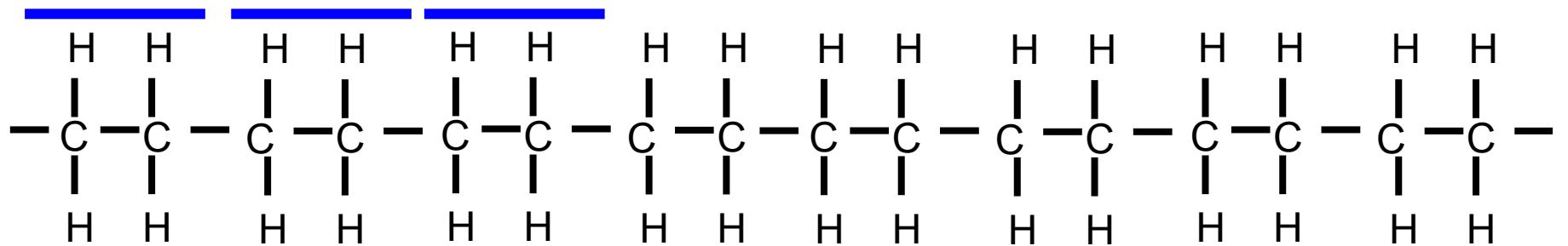
Linear chains exist, but more realistically:
Rotational degree of freedom

R

$\vec{r}_i$

N=12

l $\vec{l}$
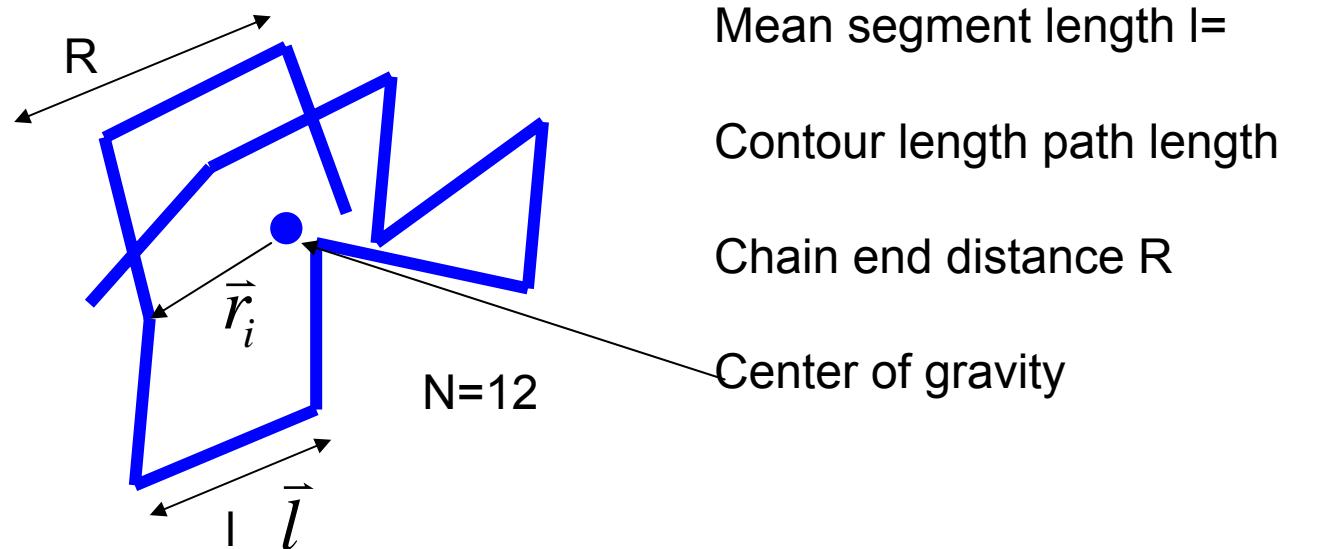
Mean segment length l=

Contour length path length $L = 12 \cdot \left| \vec{l} \right|$

Chain end distance R

Center of gravity

The polymer chain

End-to-end distance: $R = \sqrt{N} \cdot \sqrt{\left\langle \left| \vec{l} \right|^2 \right\rangle} = \sqrt{N} \cdot l$

$$R_G = \sqrt{\frac{1}{M} \sum_1^N \left\langle m_i \vec{r}_i^2 \right\rangle}$$

M mass of macromolecule
m_i mass of segment

Mean over all configurations

Radius of gyration (for a gaussian, uncorrelated chain)
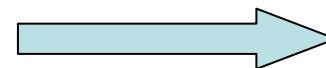
Measure for extension of macromolecule

Relation between R_G and R $\qquad R_G^{\,2} = R^2 / 6$

Using $\quad \vec{r}_i = \vec{r}_0 + \vec{l}_i = \vec{r}_i^{\,'} - \vec{r}_{CM}$
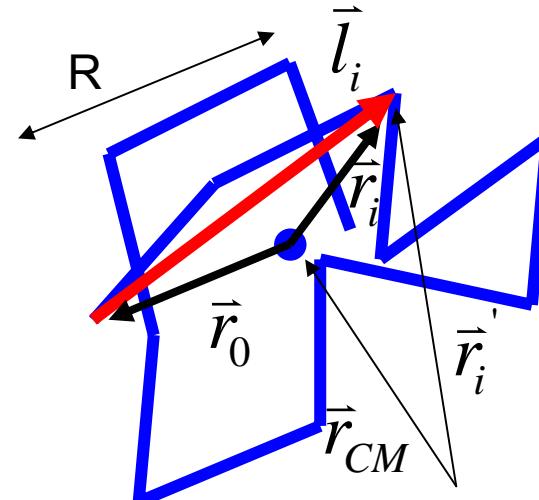
We will need this for small angle x-ray scattering!

Architectures
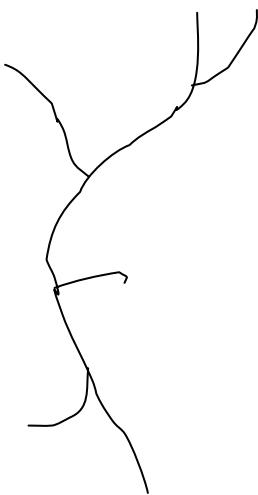
Short chain and
Long chain branches
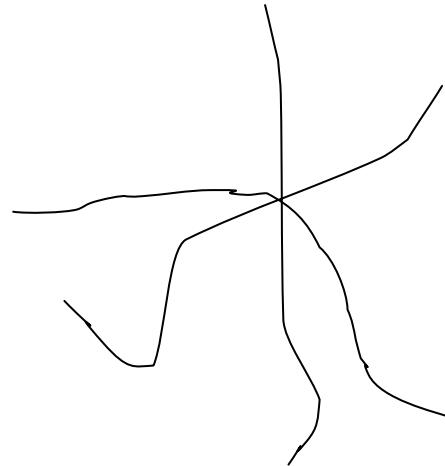
Star polymers
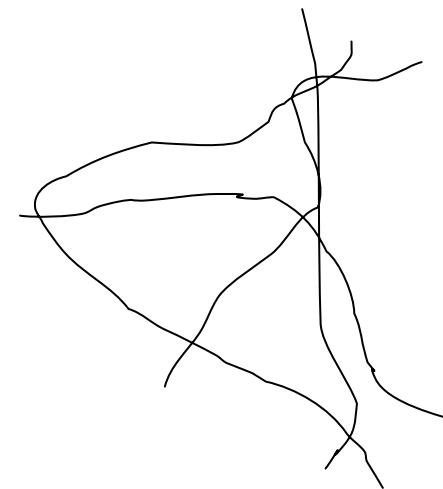
Network of cross-
linked chains

Polymerization methods


Source: Strobl
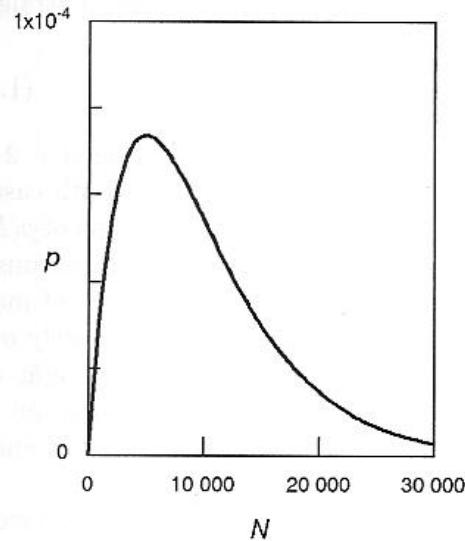
Schulz-Zimm
Step polymerization
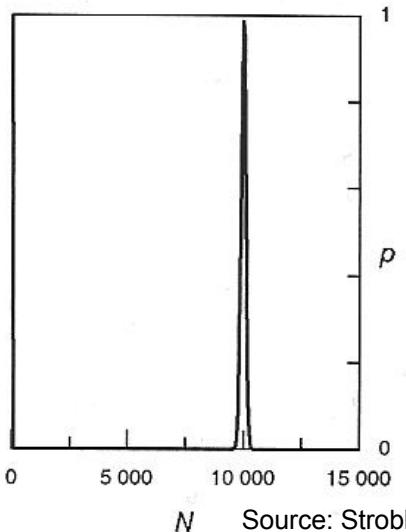
Poisson
chain polymerization

Equal degree of polymerization
Same $\overline{p}$

$$\overline{p} = \frac{\overline{M}_n}{M_0} = 10^4 \longleftarrow$$

Mass of an individual
molecule
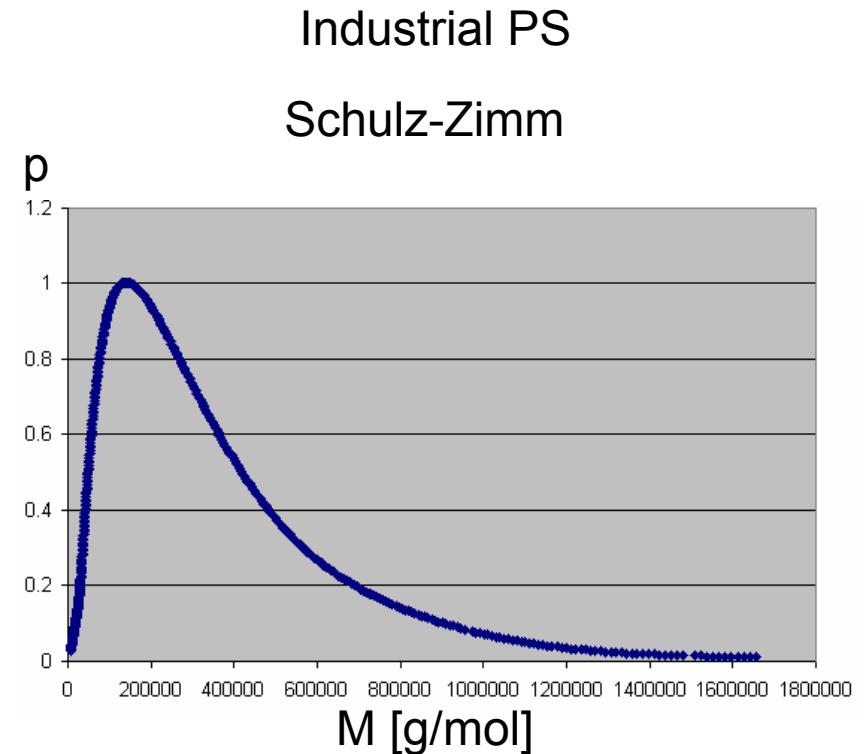
Industrial PS

Schulz-Zimm


M [g/mol]

$$\overline{M}_n = 195117$$
$$\overline{M}_w = 370820 \, g/mol$$

Polymerization methods

Establishing of covalent bonds

Chain polymerization

Step polymerization

$\ldots M+M_0 \rightarrow MM_0=M'$
$M' \rightarrow M'M_0$
$\ldots$

$\ldots G+G \rightarrow G'$
$G'+G \rightarrow G'G$
$\ldots$
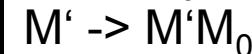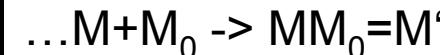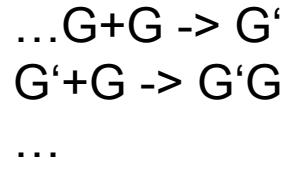
Monomeric unit (M_0)

groups of monomers (G)
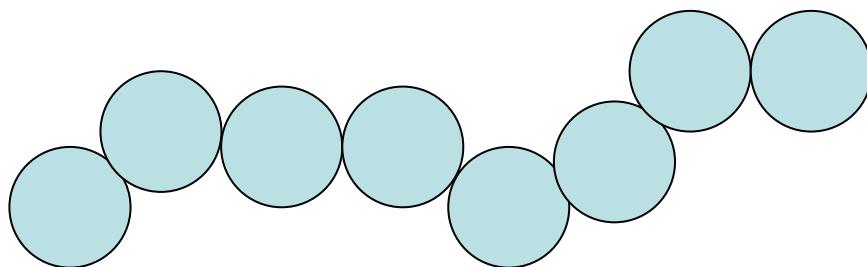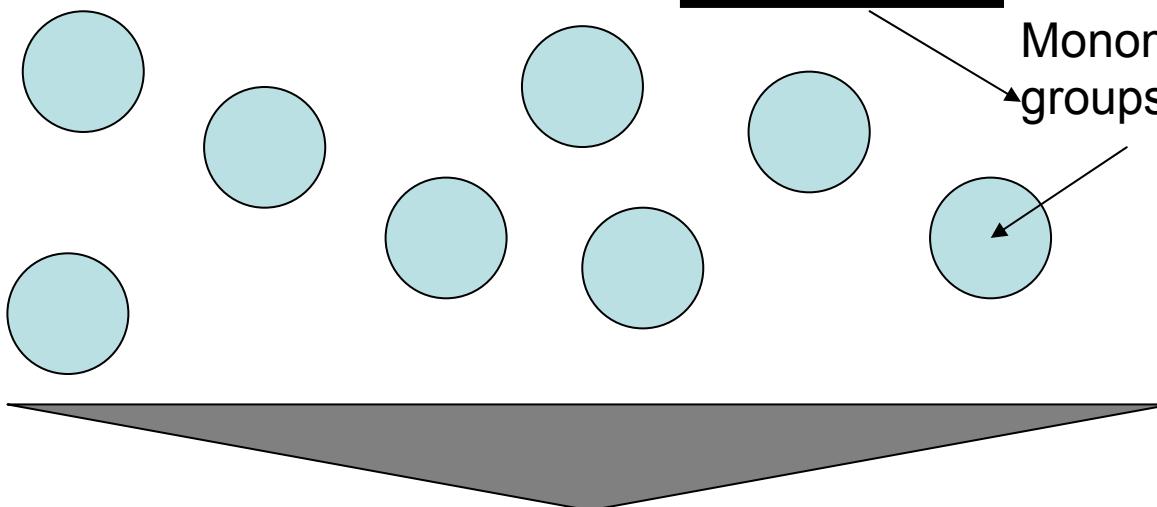
Polymerization via radicals

Well-known
Large industrial scale
Many polymers accessible

1) **Start:** Initiator I   I -> 2R•   At T, which are suitable for polymerisation

     e.g. peroxides   In-situ formation
                          light

   Many radicals start polymerization in presence of monomers (M)

   R• + M -> RM•
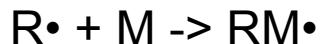
2) **Growth reaction:**   RM• + nM -> P•

3) **Stop:**   End of polymer chain growth
   Reaction of radicals at end of polymer chain

     Combination: -CH2-CHX + XCH-CH2- → -CH2-CHX-CHX-CH2-
                               Doubling of polymerization degree

     Disproportionality: -CH2-CHX + XCH-CH2- → CH=CHX + XCH2-CH2-
                               Double bond via transfer of H

Copolymers

Ethylene

$$A \quad -\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle H}{|}}{C}} - \overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle H}{|}}{C}} -$$

Propylene

$$B \quad -\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}} - \overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle H}{|}}{C}} -$$
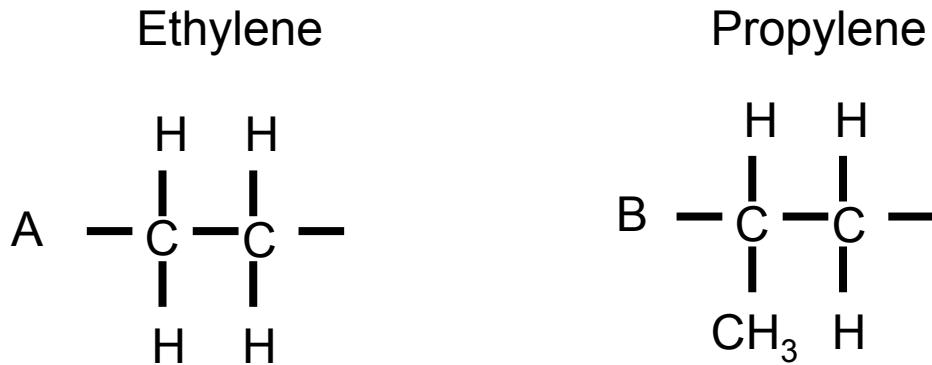
Statistical: …. ABAABBBBABAAABABAABB …

Block structure …. AAAAABBBBBAAAAABBBBB…

„A_n-block-B_m"
n,m>10

„Block-copolymers" – we will see a variety of structure, especially in thin films

Di-, tri-, multiblock copolymers

e.g.: A hard, B viscous (depending on Tg)

Glass transition temperature

… more during part II, summer semester lectures (Hermann Franz)

Brief introduction – important to understand structure of thin films!

Crystalline (lectures by AM)

Melt (liquid state) $\longrightarrow$ Solid

Cubic
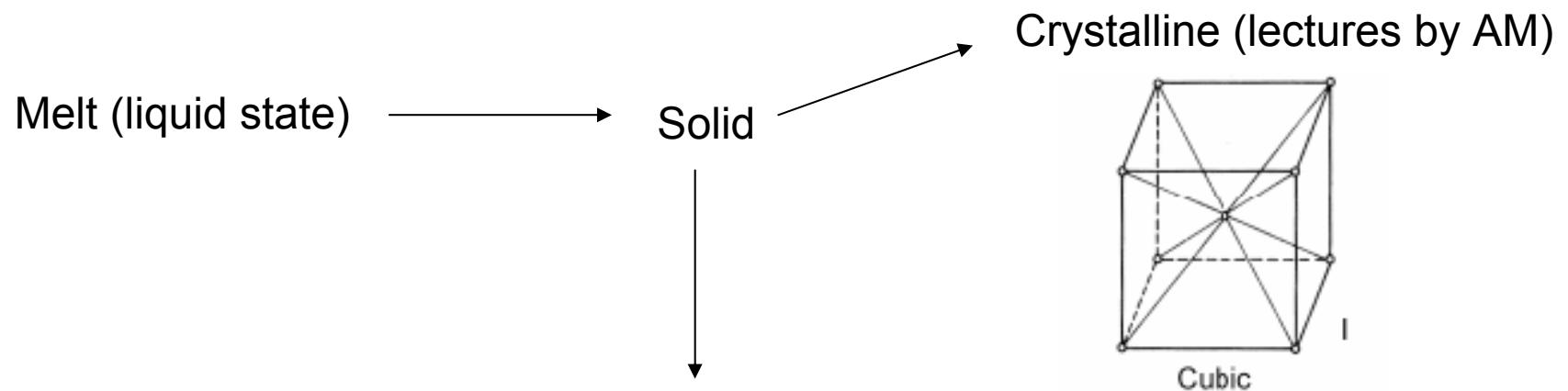
Amorphous : „frozen in liquid state", glassy
-> isotropic
-> physical parameters not direction dependent

Glass transition temperature

Howto characterize glassy state:

Characteristic temperature: T_g

Not a phase transition of 1st or 2nd degree

V(T) und die Glas-
temperatur T_g zu
verschiedenen Zeiten t
für Polyvinylacetat.
(Kovacs, J.Polym.Sci.
30(1958)131)

Source: Lechner

Dynamic interpretation: α,β-relaxation
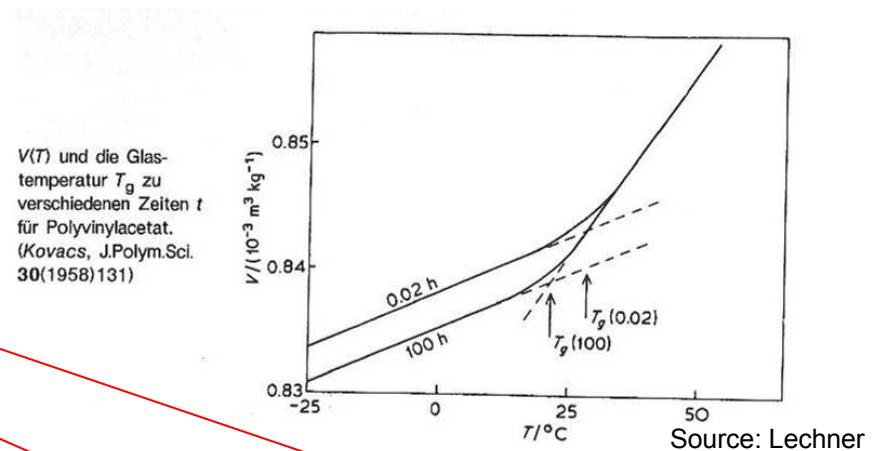
Latent heat
Melting, crystallization,…

Source: Lechner
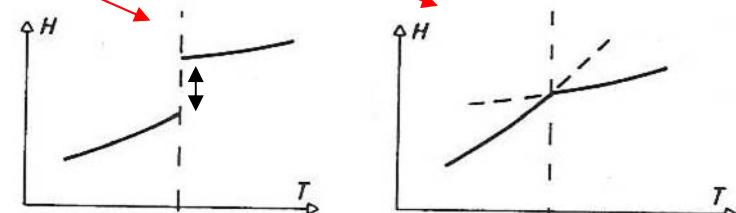
Viscoelastic:
Elastic response at small interaction times
Creep at long interaction times

Not in equilibrium, might even recrystallize

Flory-Huggins-Theory

Polymer mixtures

Polymer blends -> mixing = route to combine different materials properties

High fracture resistance and stiff
Problem: increase in elastic moduli -> brittle
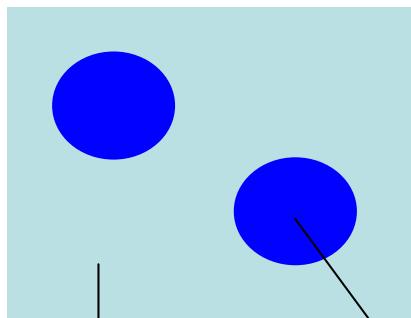
high fracture resistance
‚tough' material
Still stiff enough

Polybutadiene ~rubber

PS: stiff, but brittle

Fracture starts here and is initially localized here!

Example: (Y. Men)
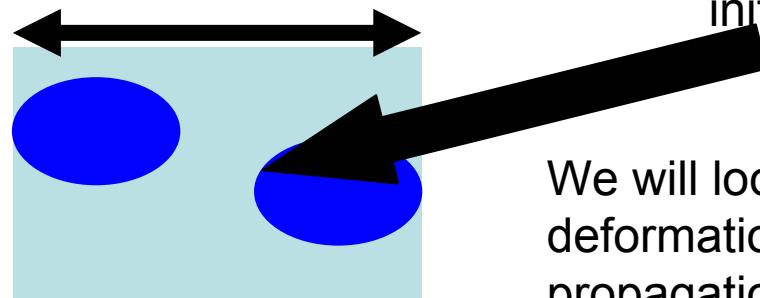
We will look with SAXS into deformation and crack propagation!

Flory-Huggins-Theory

Q: when do we obtain a homogenous or heterogenous morphology during blending?

A: Flory-Huggins theory – phase diagrams as function of T and M:

When can we expect single, binary… phases

n_A	n_B		n_A $\qquad n_B$
V_A	V_B	$\Rightarrow$	$V_A + V_B$
G_A	G_B		G_{AB}

Consider liquid state
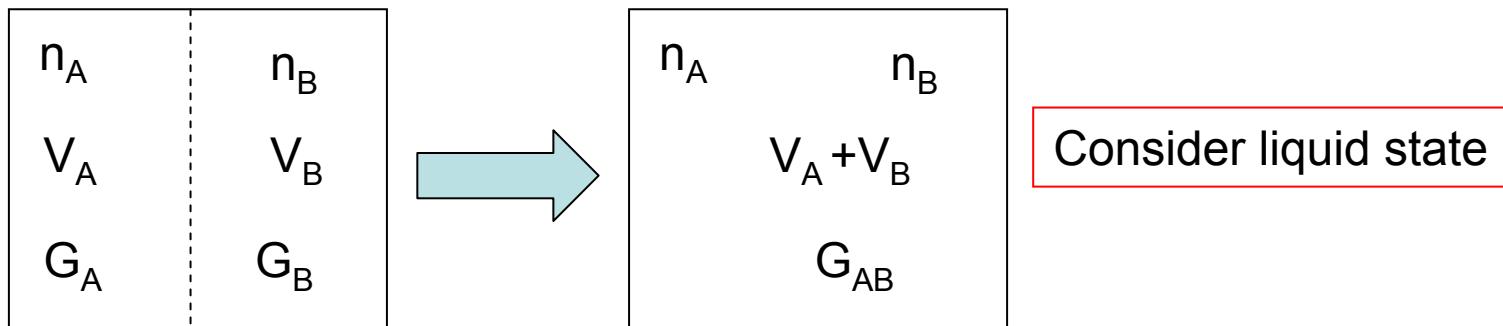
Reminder:
$$dG = -SdT + Vdp + \underbrace{\mu dN} + \gamma dA$$

Change in composition

S… entropy
μ… chemical potential (keyword: diffusion), change in phase: equilibrium µ1=µ2
γ… surface tension (2D)

For mixing:
$$\Delta G_{mix} = G_{AB} - (G_A + G_B)$$

Flory-Huggins-Theory

It states:

$$\Delta G_{mix} = -T\Delta S_t + \Delta G_{loc}$$

Change in entropy:
Mixing -> increase

Associated with motions of center of mass of all polymer molecules

+ : favours mixing

Change of local interactions and <u>motion</u> of monomers

General rule: Van-der-Waals interactions -> attractive energies between equal monomers are stronger than between different ones

- : unfavorable for mixing

Change in V: Shrinking, expansion

Formulas?

Flory-Huggins-Theory

$$\Delta G_{mix} = -T\Delta S_t + \Delta G_{loc}$$

1) $$\Delta S_t = Rn_A \ln \frac{V}{V_A} + Rn_B \ln \frac{V}{V_B} \qquad \phi_{A,B} = \frac{V_{A.B}}{V}$$

$$\Delta S_t = -Rn_A \ln \phi_A - Rn_B \ln \phi_B$$

Assumption: Polymer chains ~ ideal gas

2) $$\Delta G_{loc} = RT \frac{V}{v_C} \chi \phi_A \phi_B \qquad v_C$$

v_C Molar volume of a reference unit common to A and B

„The higher the concentration, the more likely the interaction"

χ Flory-Huggins-Parameter

Empirical parameter
Nearest neighbour interactions
„contact energies"

This makes sense:
$$\Delta G_{loc} \to 0$$
$$\phi_A, \phi_B \to 0$$

Flory-Huggins-Theory

$$\Delta G_{mix} = -T\Delta S_t + \Delta G_{loc}$$

$$\Delta G_{loc} = RT \frac{V}{v_C} \chi \phi_A \phi_B$$

Derivation general for solid state physics!

Now one A-chain in mixture

A B

Number of nearest neighbours: z
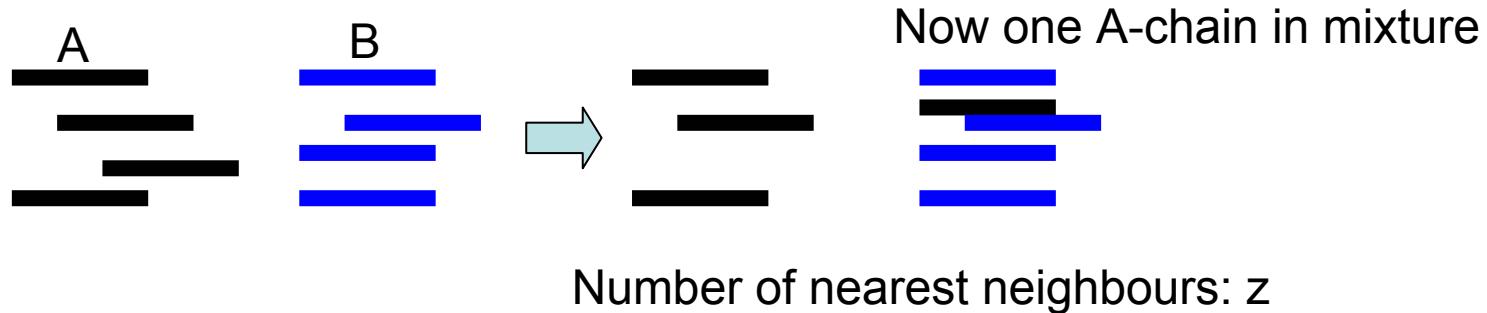
Hence: Increase in potential energy: $\dfrac{z}{2}\phi_B kT \chi'$

Avoid double counting

Increase in G only when AB-pair is formed –> probability: ϕ_B

Energy increase by dimensionless parameter: χ' with respect to kT

Hence: $$\Delta G_{loc} \sim kT \frac{z}{2} \chi (\phi_A \phi_B + \phi_B \phi_A)$$

Phase diagrams

$$\Delta G_{mix} = RTV\left(\frac{\phi_A}{v_A}\ln\phi_A + \frac{\phi_B}{v_B}\ln\phi_B + \frac{\chi}{v_C}\phi_A\phi_B\right) \qquad v \quad \text{Molar volume}$$

Low molar mass -> entropy leads to mixing

Polymers: large molecular weights $\quad v_{A,B}\to\infty \qquad \Delta S_t \to 0$

Mixing takes place, when ΔG_{mix}<0

$$\chi < 0 \quad \text{Mixing!} \qquad \chi > 0 \quad \text{incompatibility}$$

Symmetric mixture: Equal degree of polymerization

$$N_{A,B} = \frac{v_{A,B}}{v_C} \qquad N_A = N_B = N \qquad \phi_A + \phi_B = 1$$

$$\Delta G_{mix} = RT(n_A + n_B)\left(\phi_A\ln\phi_A + \phi_B\ln\phi_B + \boxed{\chi N}\phi_A\phi_B\right)$$

Phase diagrams

Symmetric binary polymer mixture

$$\phi_A = 0.45$$ 2.8 Critical point

Homogenous AB-mixture

$\phi_A{}'$ 2.4 $\phi_A{}''$

Miscibility gap

2.0

1.6 χN

ϕ_A

$\Delta G_{mir} / R\breve{T}(n_A + n_R)$
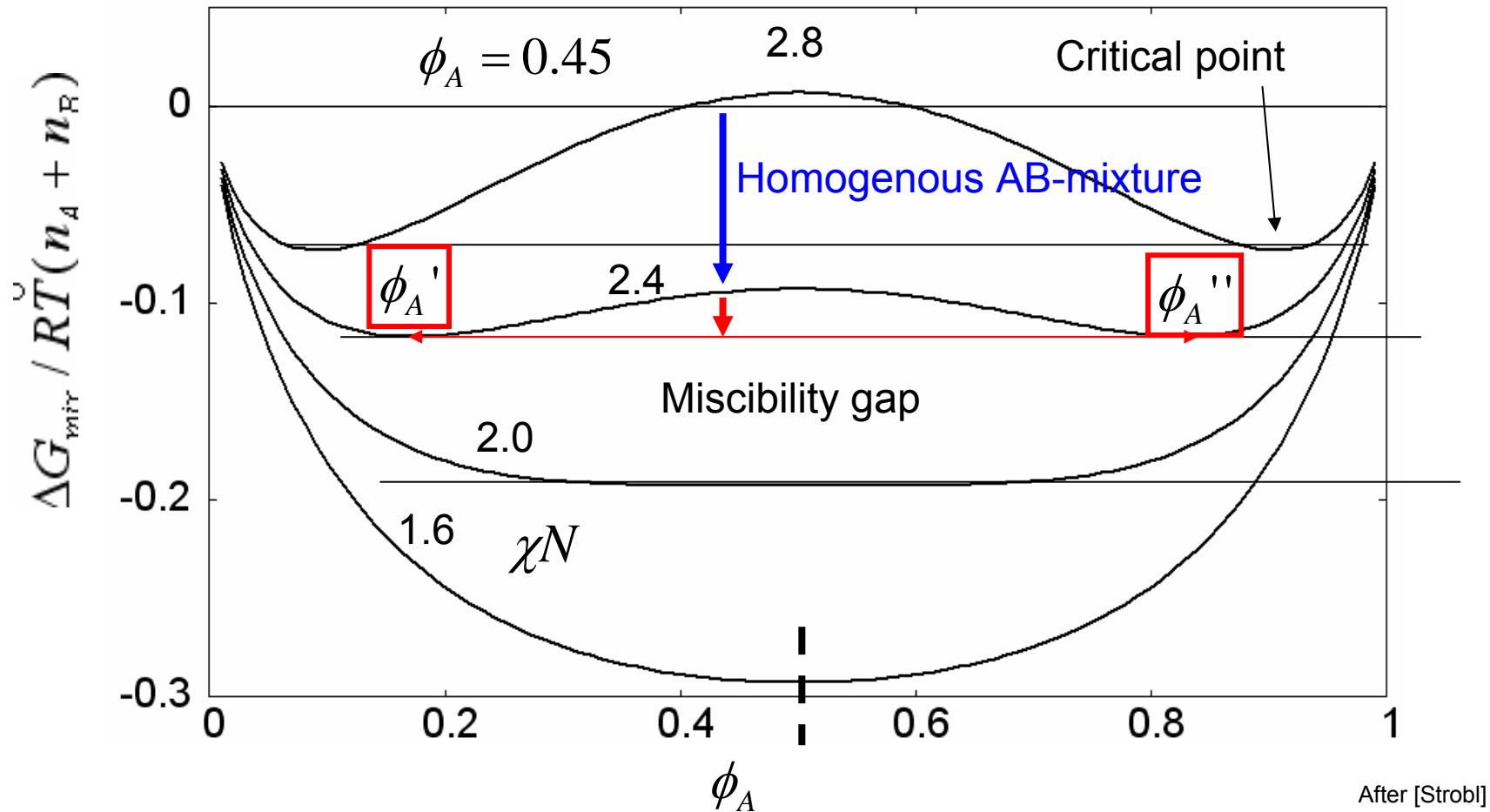
After [Strobl]

$$\phi_A{}' < \phi_A < \phi_A{}''$$ Two phases, demixing

Phase diagrams

Consequences $\dfrac{\partial^2 \Delta G_{mix}}{\partial \phi_A^{\,2}}\Bigg|_{\phi_A=0.5} = \dfrac{1}{\phi_A} + \dfrac{1}{1-\phi_A} - 2\chi N = 0$ Vanishing curvature

$\chi N = 2$ Critical value: separates region with miscibility gap

$\chi < \chi_C = \dfrac{2}{N}$ Compatibility through all concentrations, mixing

$\chi > \chi_C$ Miscibility gap $\longrightarrow$ N>>0 $\chi > 0$ No mixing for high molecular weight!

Critical concentrations

$\dfrac{\partial \Delta G_{mix}}{\partial \phi_A} = 0$

χN

Universal!

ϕ_A
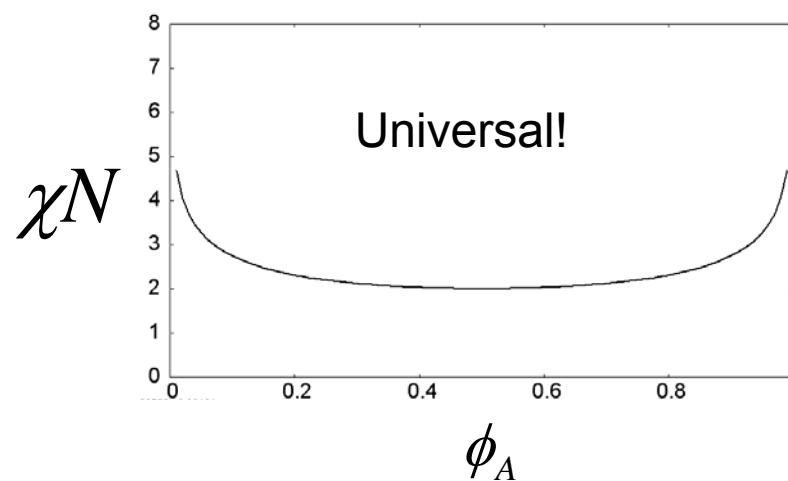
Phase diagrams

In general: upper and lower miscibility gap possible

Include T, one can show (thermodynamics!):

$$\Delta G_{loc} = \Delta H_{mix} - T\Delta S_{loc}$$

Endo- or exotherm : >0 or <0

$$\chi \sim \frac{1}{T} \qquad \chi = \frac{2}{N}\frac{T_C}{T} > 0$$

Entropic contributions to ΔG_{loc} (‚mobility') neglected

Endothermal polymer mixture

miscibility for high temperatures, if molecular weights low enough

-> mobile enough!

Of course, inverse for exothermal…
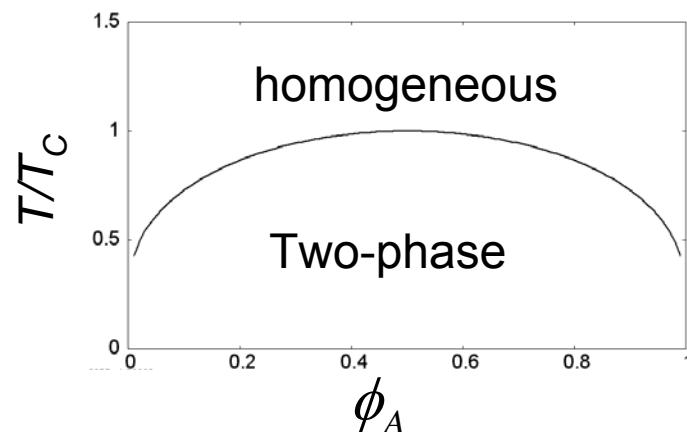
Partial crystalline polymers

PS -> glassy solidification during cooling: no long range order

PE, PP, PA: long range order -> building-up of lamellar block

Lamellae, ~nm
Periodic arrangement

amorphous

Ordered region

$W<<B$

B

SAXS-pattern

[Schroer, Appl. Phys. Lett (2006)]

Why? Cooling –> reduced mobility -> no thermodynamic equilibrium ->multiple folding of polymer chains
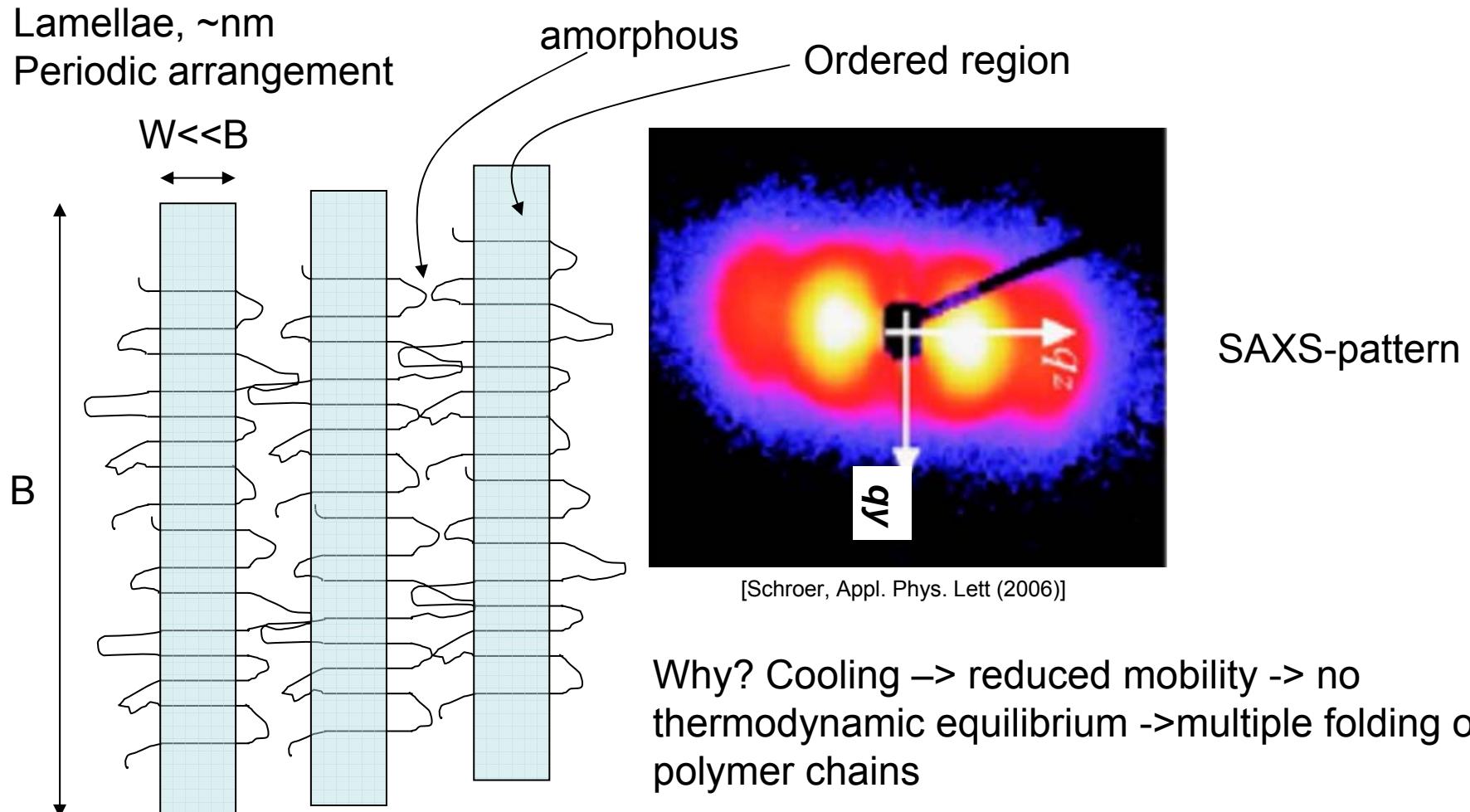
Block Copolymers

"2 different species couples together by a chemical link" [Strobl]

We learn from Flory-Huggins-Theory:

binary polymer mixture -> separation in 2 phases

…. AAAAABBBBBAAAABBBBB…

↑

Linkage ~phase separation

→ microphase separation: mesoscopic domains: nm…100nm >> single block

→ domains: uniform size, arrangement!

→ continous phase possible

AAAAABBBBB

A-Spheres A-Cylinders OBDD Lamellae OBDD B-Cylinders B-Spheres [Strobl]

0.17   0.28   0.34   0.62   0.66   0.77   PS-b-PI
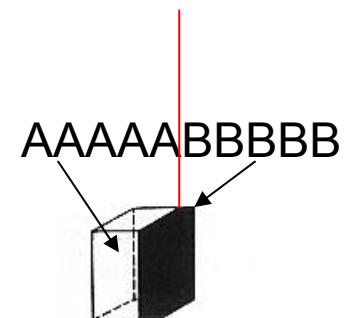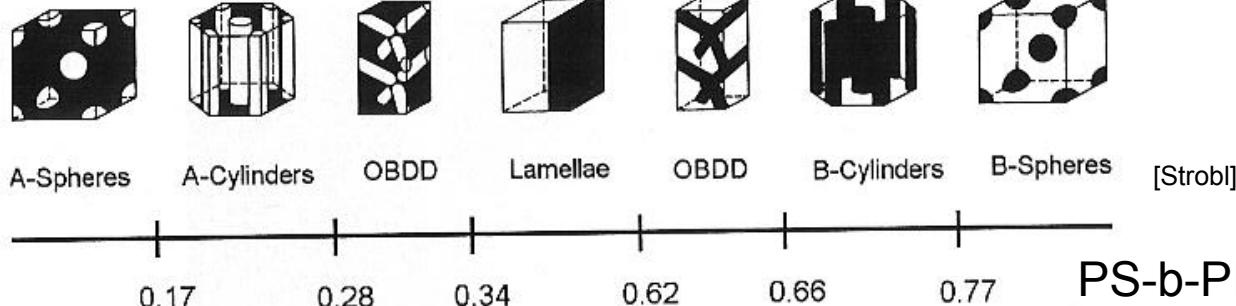
→ this is already a nanocomposite

→ Applications: Solar cells, magnetic data storage, masks, lithography, nanowires…

Colloids

- Polymers
- Metals

- Small particles, dispersed in liquid phase
- Size: nm….µm
- Wall paintings
- Polymers: Spheres

Production: [Xia, Adv. Mat. (2000)]

Emulsion polymerization: Example latex particles (styrene/butadiene)

1. Initiator (e.g. Potassium-persulfat) -> dissolved in water: Burst of free radicals -> polymerize monomers: nuclei

2. Surfactant: Micelles, swollen by monomer
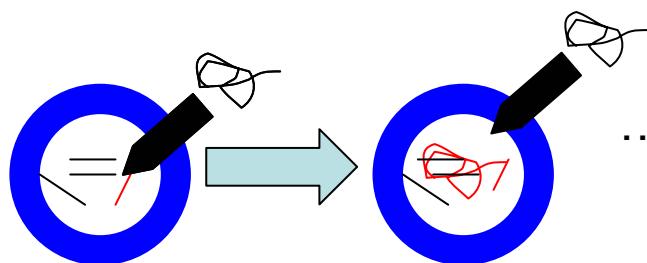
…until all monomer consumed:
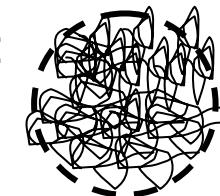
Colloids

… and you obtain nice spheres: … which you can nicely arrange here in 2D:
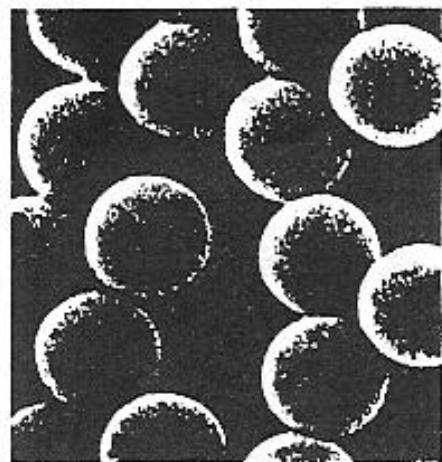
[Springer]
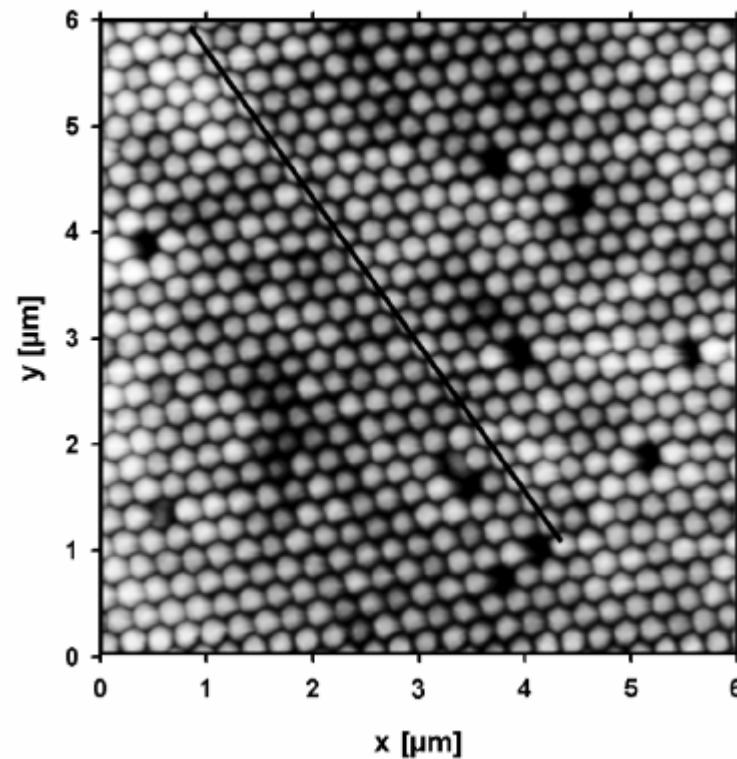
[Frömsdorf, J. Chem. Phys. (2006)]

Methoden moderner Roentgenphysik I - Vorlesung im Haupt/Masterstudiengang Physik, Universität Hamburg, WS 2008/9 S.V. Roth

Application

Optical properties: sharp resonances ⟺ plasmon resonances
(visible light)   cluster arrangement & shape
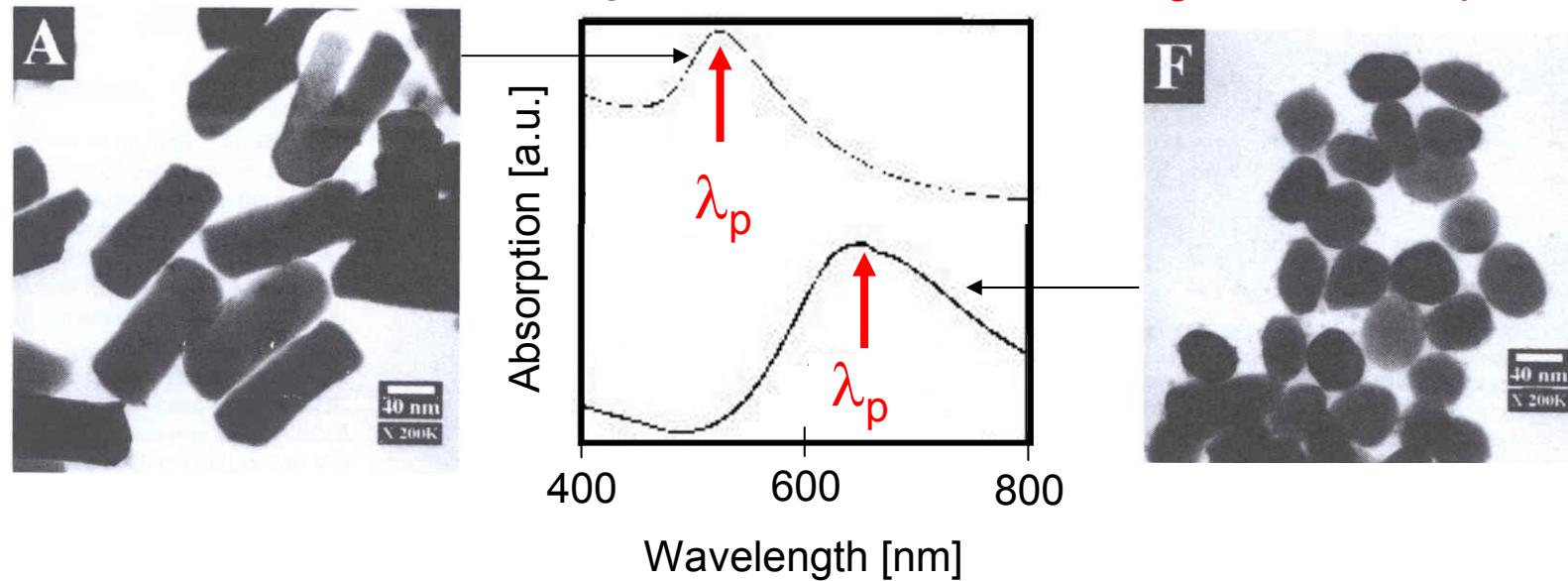

J.C. Hulteen et al., J Phys. Chem. B 101, 7727 (1997)

Colloids – Gold, Silica, Fe, CoPt, etc…

Simple recipies: Bauer, Nanotechnology (2003)

(1) 0.01% (w/v) tetrachloroauric[III]acid trihydrate
(**HAuCl4·3H2O** in 100 ml of water) is heated to boiling.
(2) 1 ml of 1% (w/v) **trisodium citrate dihydrate** is added to
the boiling solution under constant stirring.
(3) In about 25 s the slightly yellow solution will turn faintly
blue (nucleation).
(4) After approximately 70 s the blue colour then suddenly
changes to dark red, indicating the formation of
monodisperse spherical particles.
(5) The solution is boiled for another 5 min to complete
reduction of the gold chloride.

C6H5Na3O7•2(H2O)

Au Au
Au Au   + byproducts (salts)
   Au
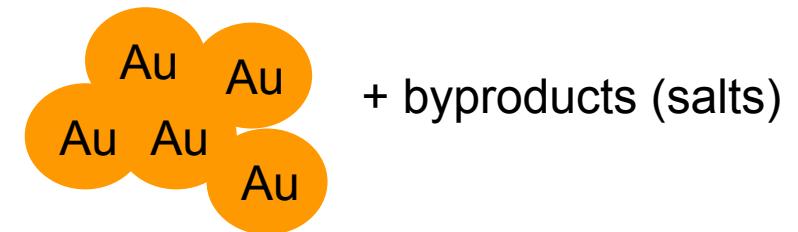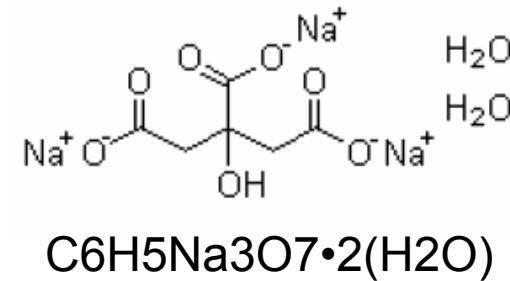
More structures: Core-Shell:

[Abul Kashem, Macromolecules (2008)]
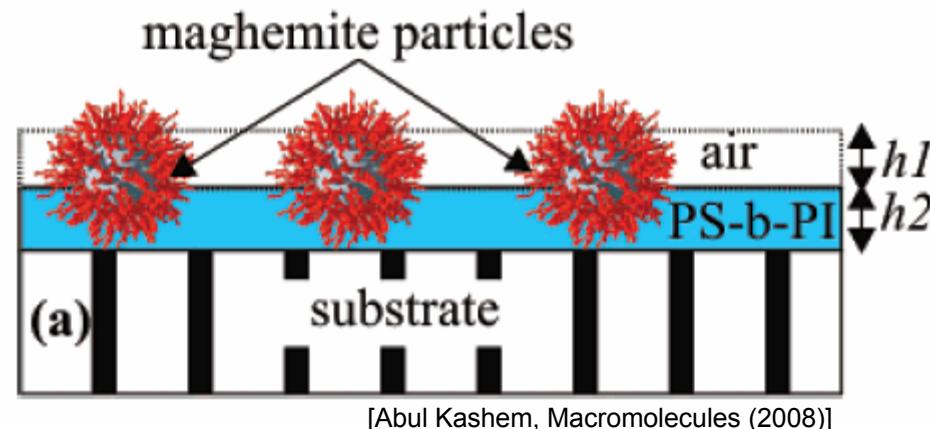
Polymer-Metal Nanocomposites


Biswas et al., Vac. Tech. Coat. **7**, 54 (2006).
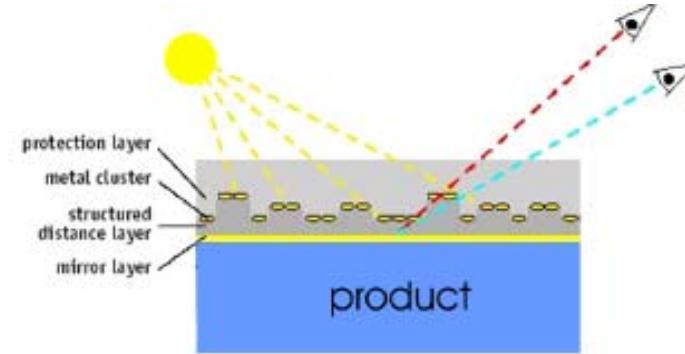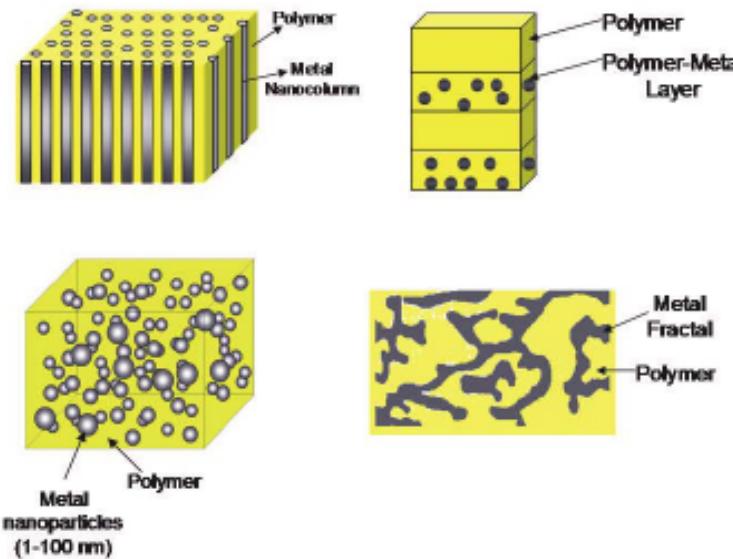
Bauer et al., Nanotechnology 14,1289 (2003)

14°   90°
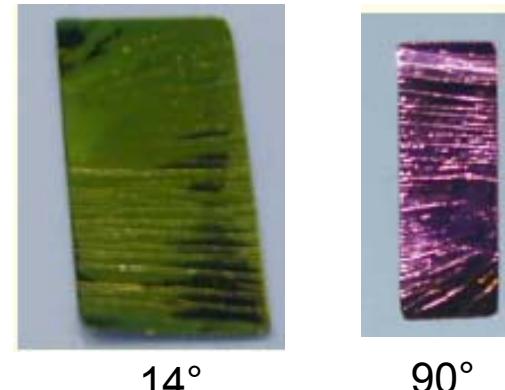
High-frequency filters
**Solar cells**

$v_{lim} \sim \rho/R^2$

Anti-counterfeiting
Biosensors

Polymer-Metal Nanocomposites: Production

Sputter deposition:

Ar$^+$

Substrate

Height, 1 μm x 1 μm
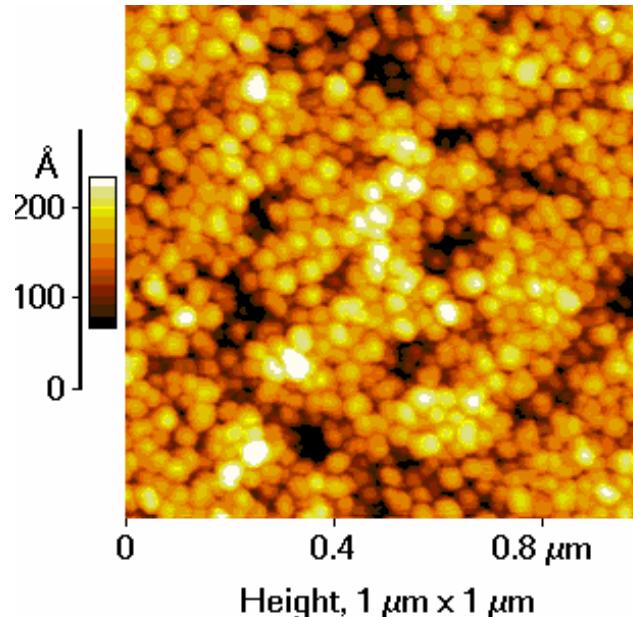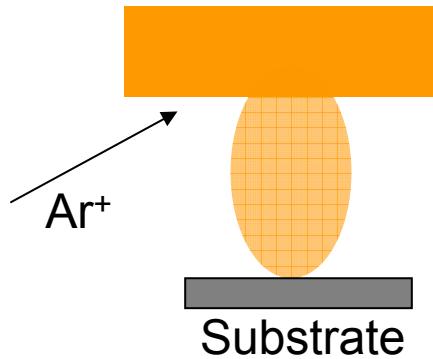
- Nice clusters, too
- Fast deposition method
- Usually broader size distribution
- self-assembly: Au-Au interaction much stronger than Au-Polymer interaction

300nm

Noble metal (Au, Ag, Cu,…)

Polymer film

Substrate (Si, glass, + TiO2)
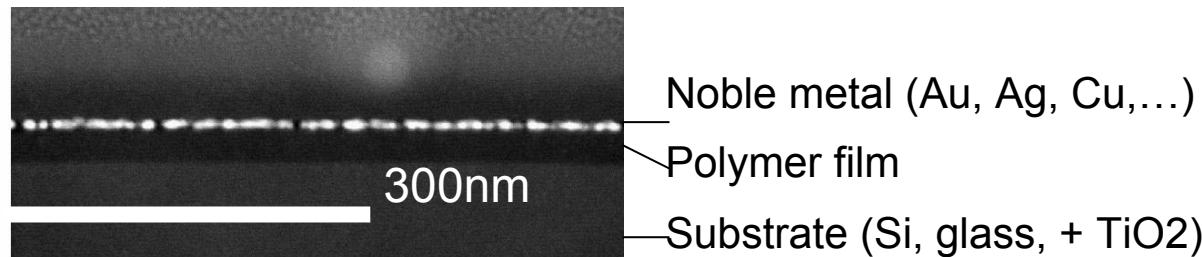
Roth et al., Appl. Phys. Lett. **88**, 021910 (2006)

Polymer-Metal Nanocomposites: Production

Sputter deposition:
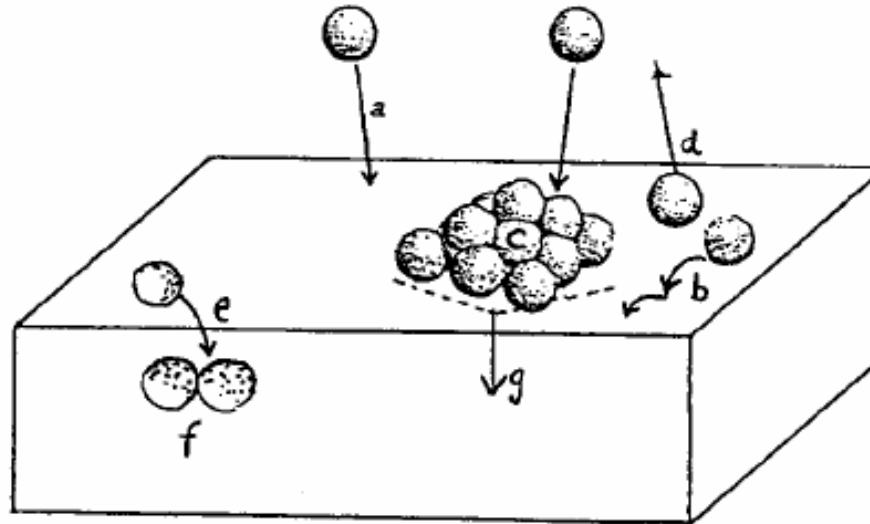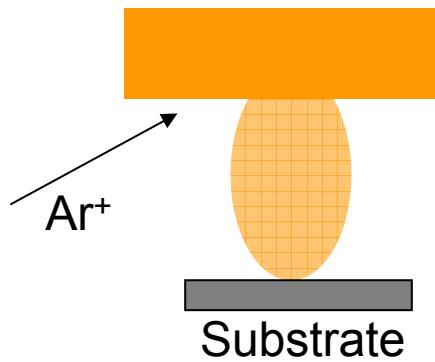
F. Faupel et al., in: Low Dielectric Constant Materials for IC Applications, P. S. Ho, W. W. Lee, and J. Leu (Eds.), Springer Verlag, 221 (2003) pp. 221

- Nucleation   - Growth   - Coalescence

Modelling of industrial process: in-situ kinetic of nanoparticle growth