Methoden moderner Röntgenphysik II:
Struktur und Dynamik kondensierter Materie

Vorlesung zum Haupt/Masterstudiengang Physik

SS 2011

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

SemRm3, Physik, Jungiusstrasse
Di: 14:00-15:30
Do: 11:20-12:50
S. V. Roth (SR)
21.4.2011, 28.4.2011 & 3.5.2011 finden statt
26.4.2011 fällt aus

Aim

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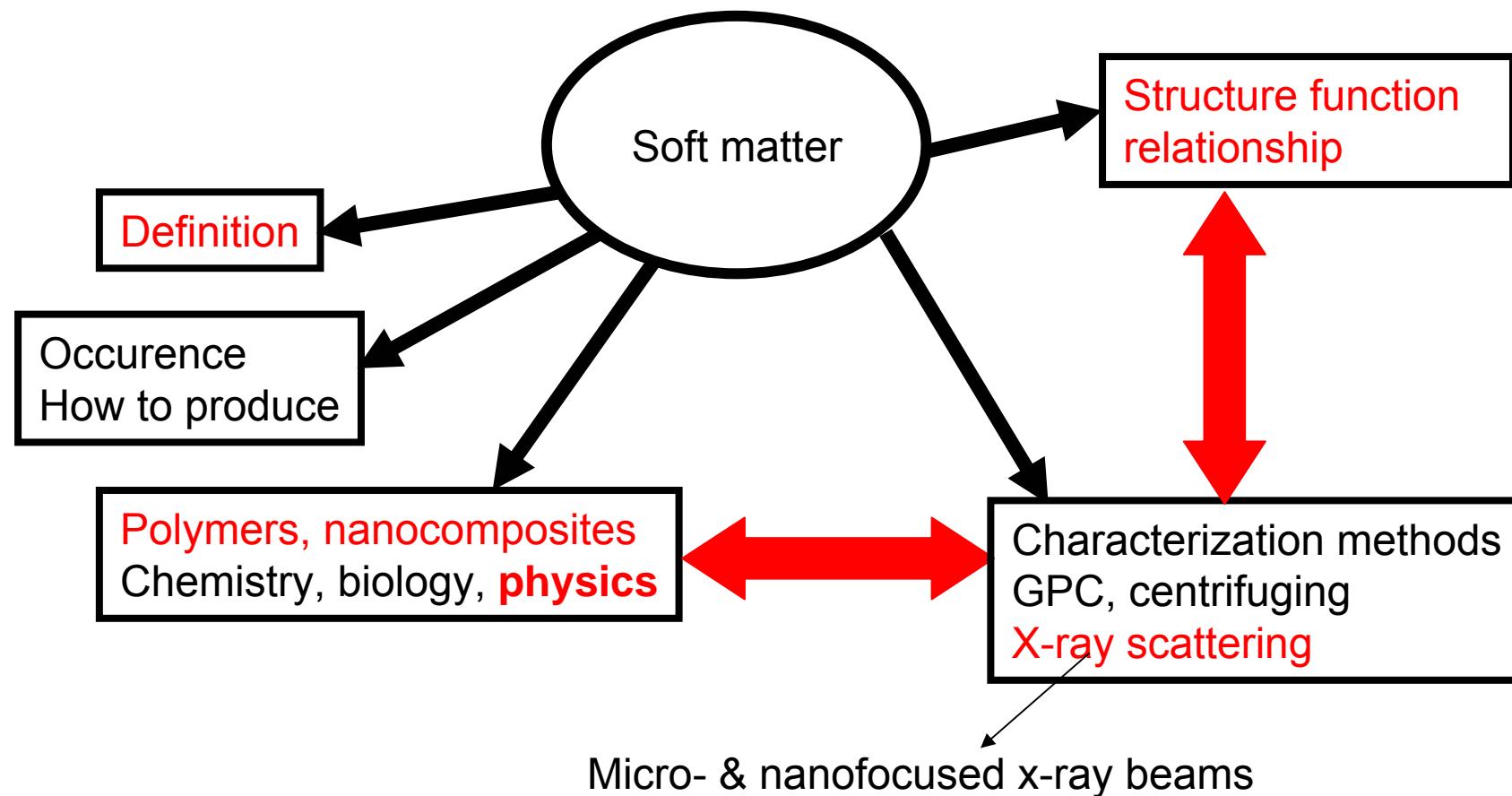
Literature

- [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

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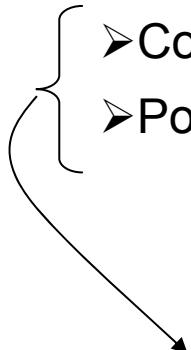
Take care – here, metals (hard matter, actually) comes into play. But it's still soft matter – this is no contradiction, as you will see!

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

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 <u>physical properties!</u>

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

Basic definition

Standard example: Polyethylene (PE)

Ethylene:
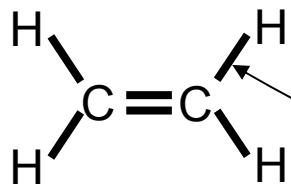
Structure unit
Monomeric unit

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

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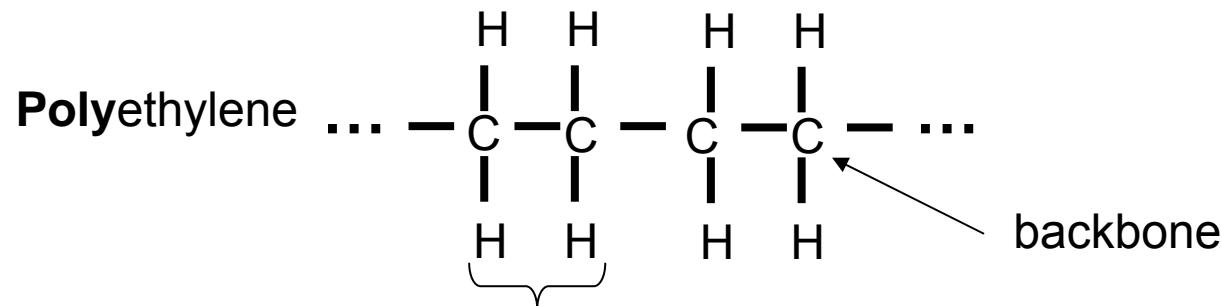
Number of monomers: Degree of polymerization: N
Polymerization process: starts from low molar mass compounds

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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

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

M_m

Source: Stribeck

0.5

0.5

M_n

Source: Stribeck

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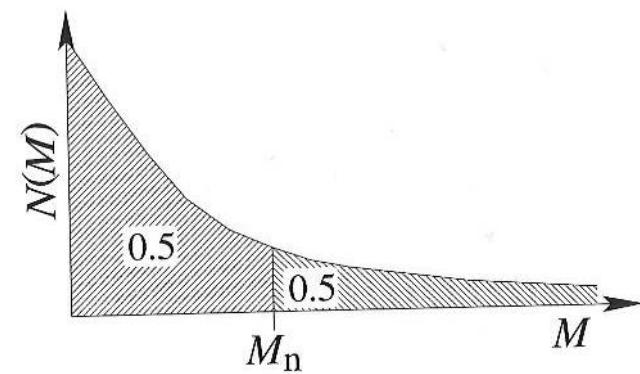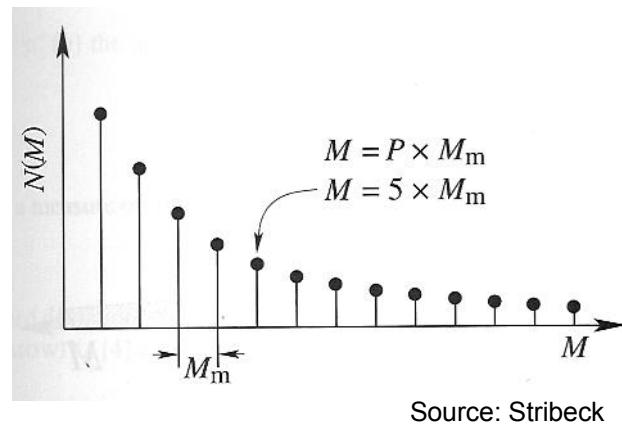
Polydispersity

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

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

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

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

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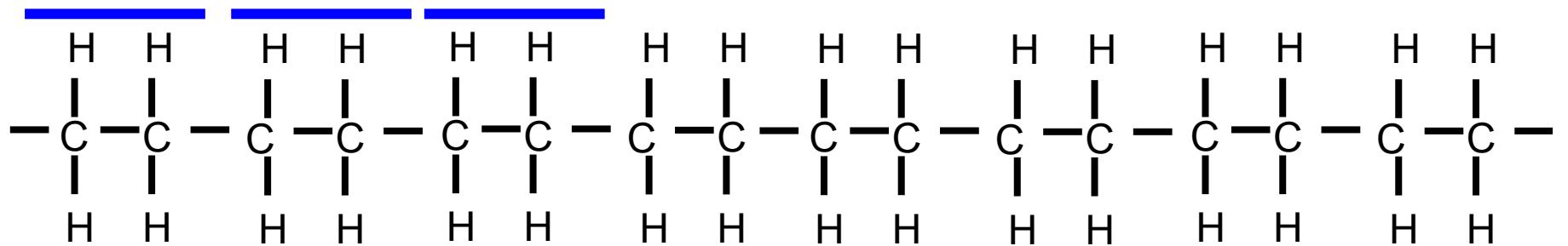
Linear chains exist, but more realistically:
Rotational degree of freedom

Mean segment length l=

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

Chain end distance R

Center of gravity
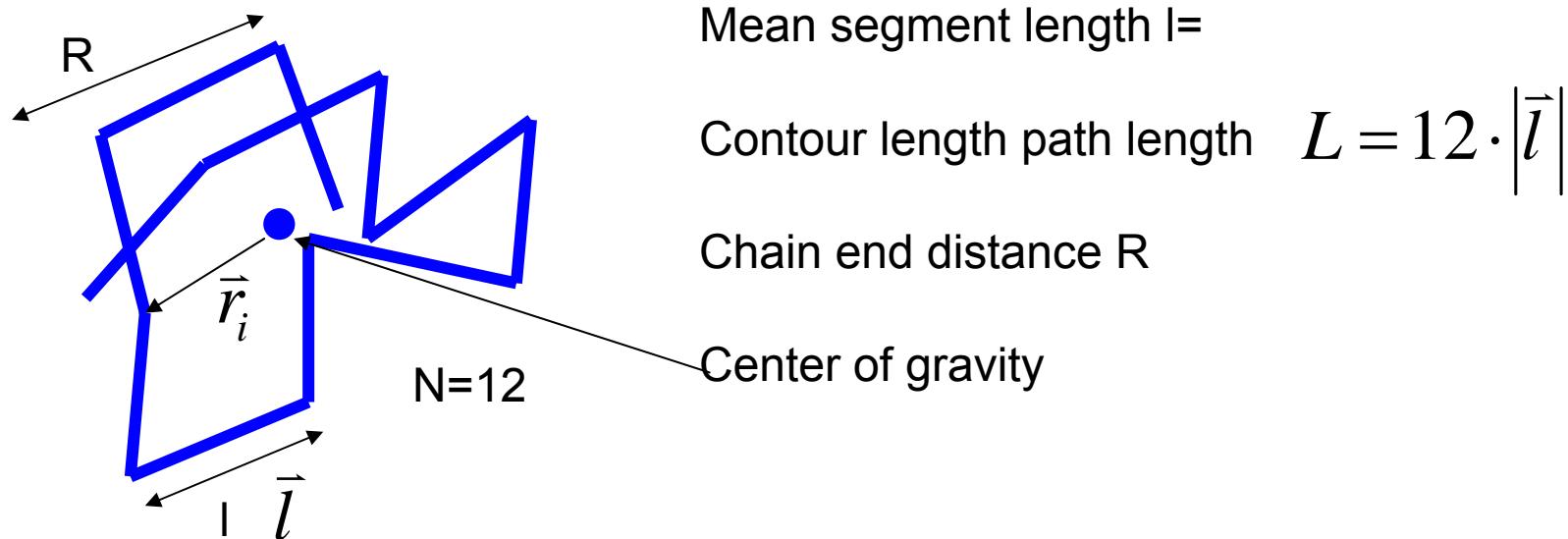
The polymer chain

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

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

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 $R_G^2 = R^2 / 6$

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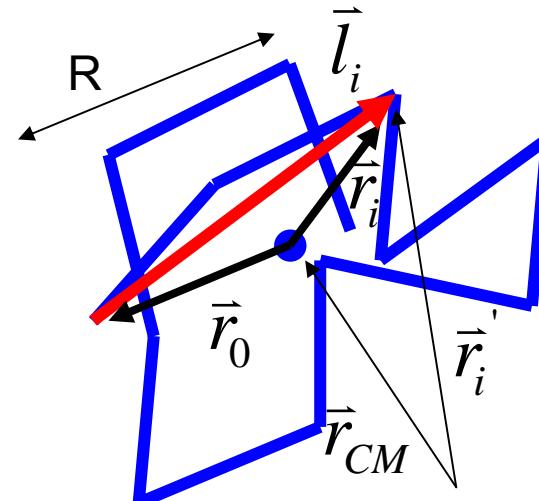
We will need this for small angle x-ray scattering!

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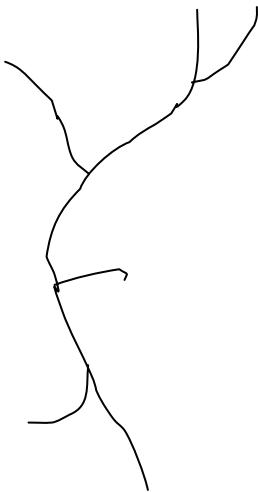
Short chain and
Long chain branches
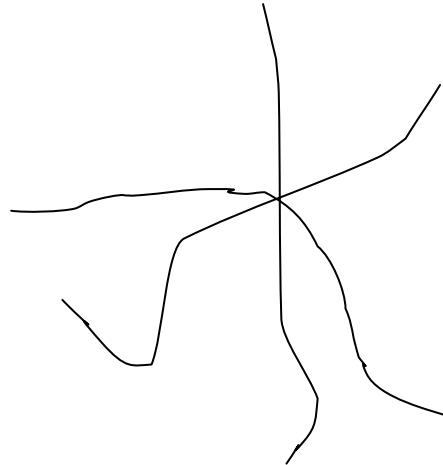
Star polymers
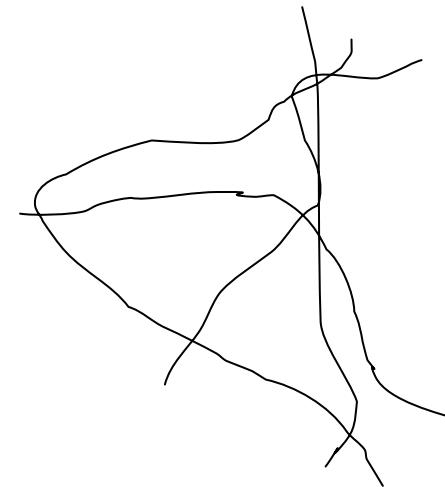
Network of cross-
linked chains

Polymerization methods

Source: Strobl
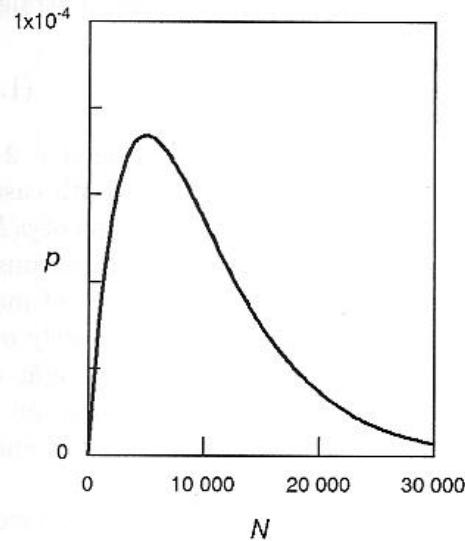
Schulz-Zimm
Step polymerization
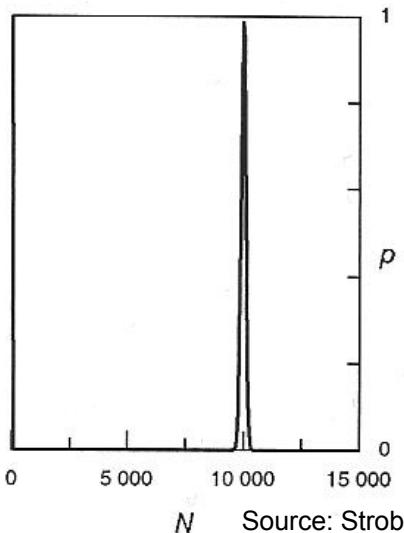
Poisson
chain polymerization

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

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

$$\ldots G+G \rightarrow G'$$
$$G'+G \rightarrow G'G$$
$$\ldots$$
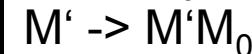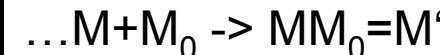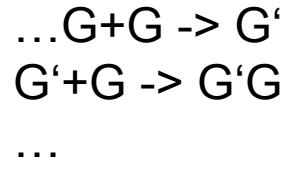
Monomeric unit (M_0)
groups of monomers (G)
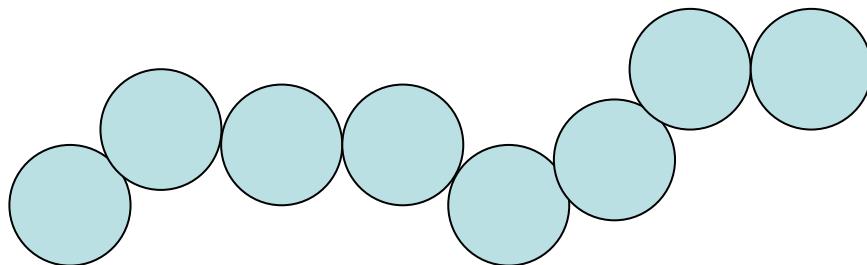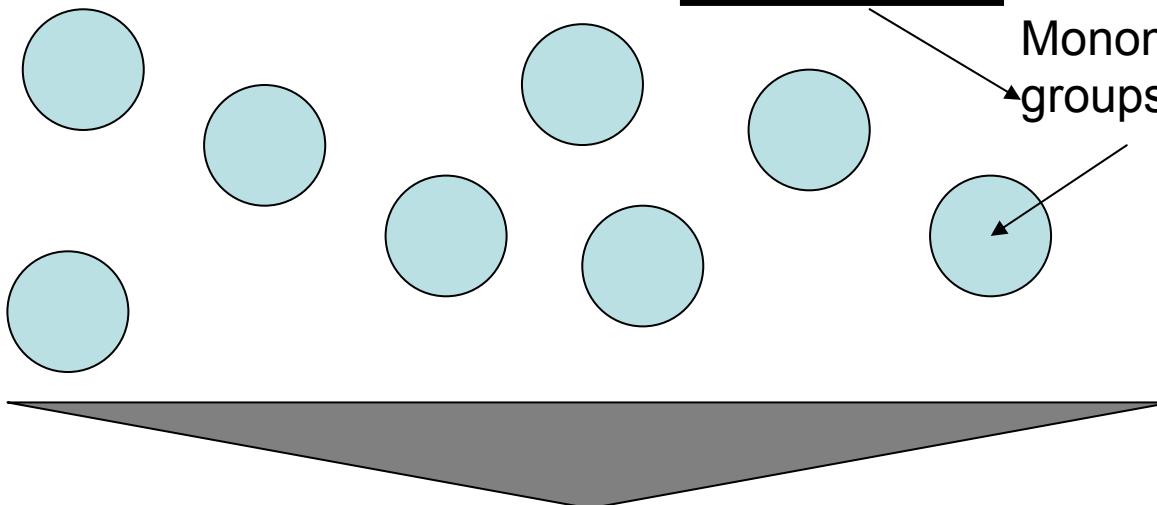
Polymerization via radicals

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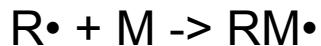
2) **Growth reaction:**   RM• + nM -> P•

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

Combination: -CH2-ĊHX + XĊH-CH2- → -CH2-CHX-CHX-CH2-
                         Doubling of polymerization degree

Disproportionality: -CH2-CHX + XCH-CH2- → C**H**=CHX + XC**H2**-CH2-
                         Double bond via transfer of **H**

Copolymers

Ethylene

Propylene
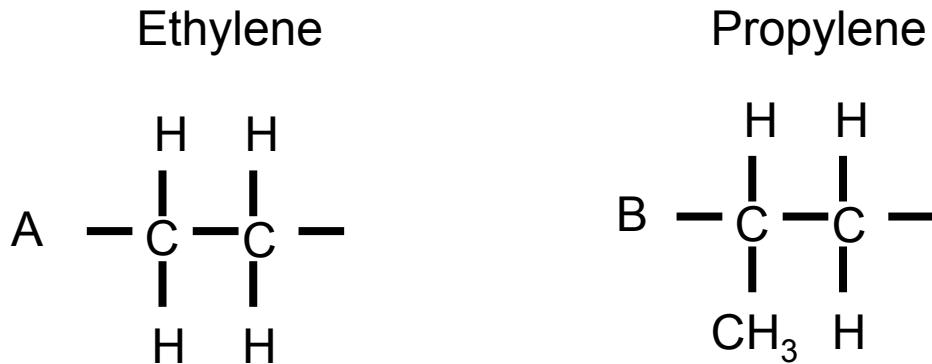
Statistical: …. ABAABBBBABAAABABAABB …

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) ⟶ Solid ⟶

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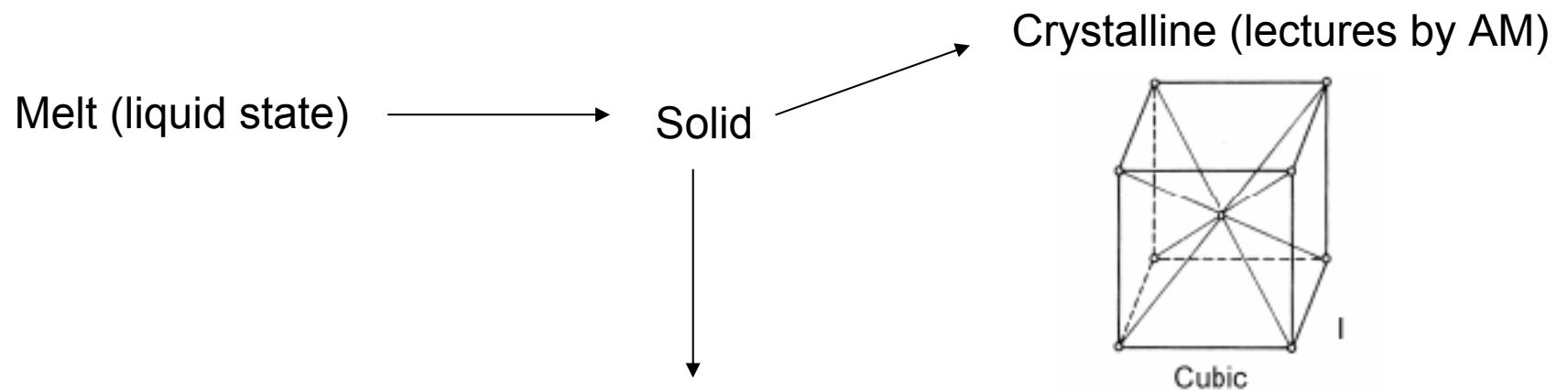
Amorphous : „frozen in liquid state", glassy
-> isotropic
-> physical parameters not direction dependent

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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
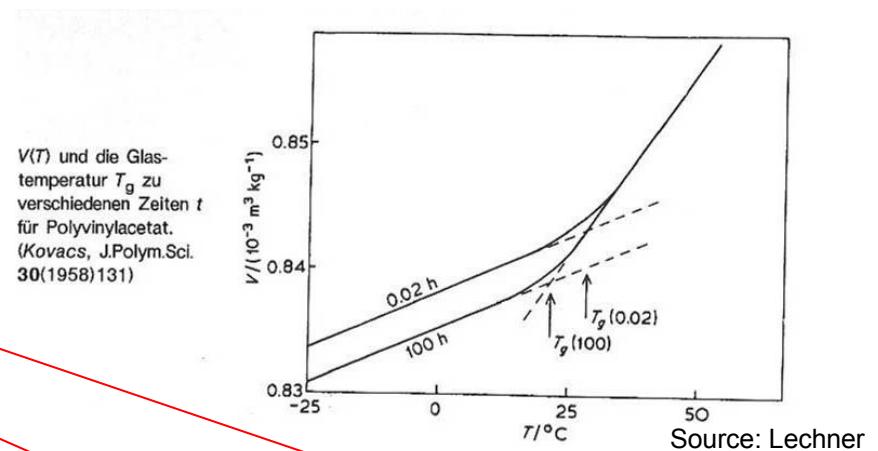
Latent heat
Melting, crystallization,…

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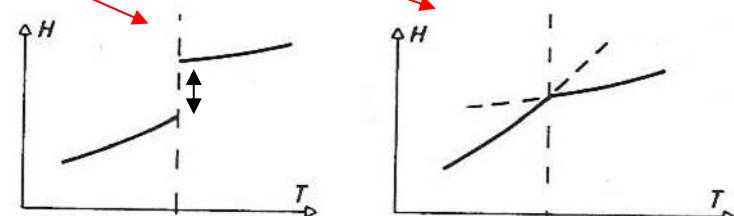
Viscoelastic:
Elastic response at small interaction times
Creep at long interaction times

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
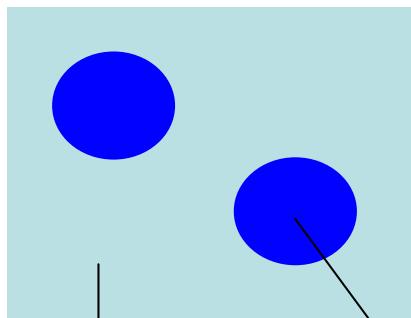
high fracture resistance
‚tough' material
Still stiff enough

Polybutadiene ~rubber

PS: stiff, but brittle

Fracture starts here and is initially localized here!

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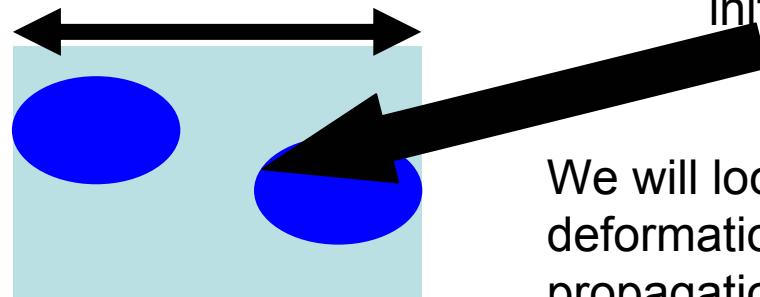
We will look with SAXS into deformation and crack propagation!

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
V_A	V_B
G_A	G_B

→

n_A	n_B
	$V_A + V_B$
	G_{AB}

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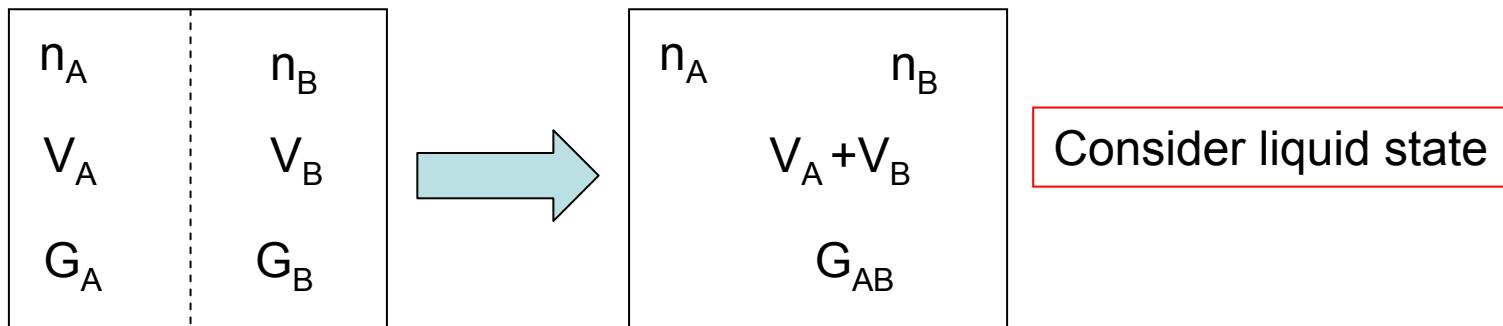
Reminder: $$dG = -SdT + Vdp + \underbrace{\mu dN} + \gamma dA$$

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)
$$\Delta G_{loc} = RT \frac{V}{v_C} \chi \phi_A \phi_B \qquad v_C \quad \text{Molar volume of a reference unit common to A and B}$$

„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
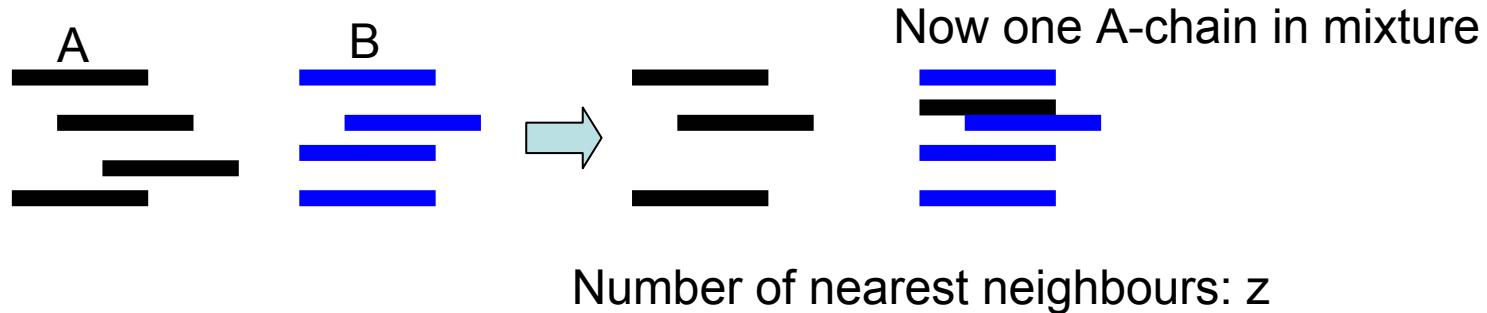
Hence: Increase in potential energy: $\frac{z}{2}\phi_B kT\chi'$

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 $v_{A,B} \to \infty \qquad \Delta S_t \to 0$

Mixing takes place, when $\Delta G_{mix} < 0$

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

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
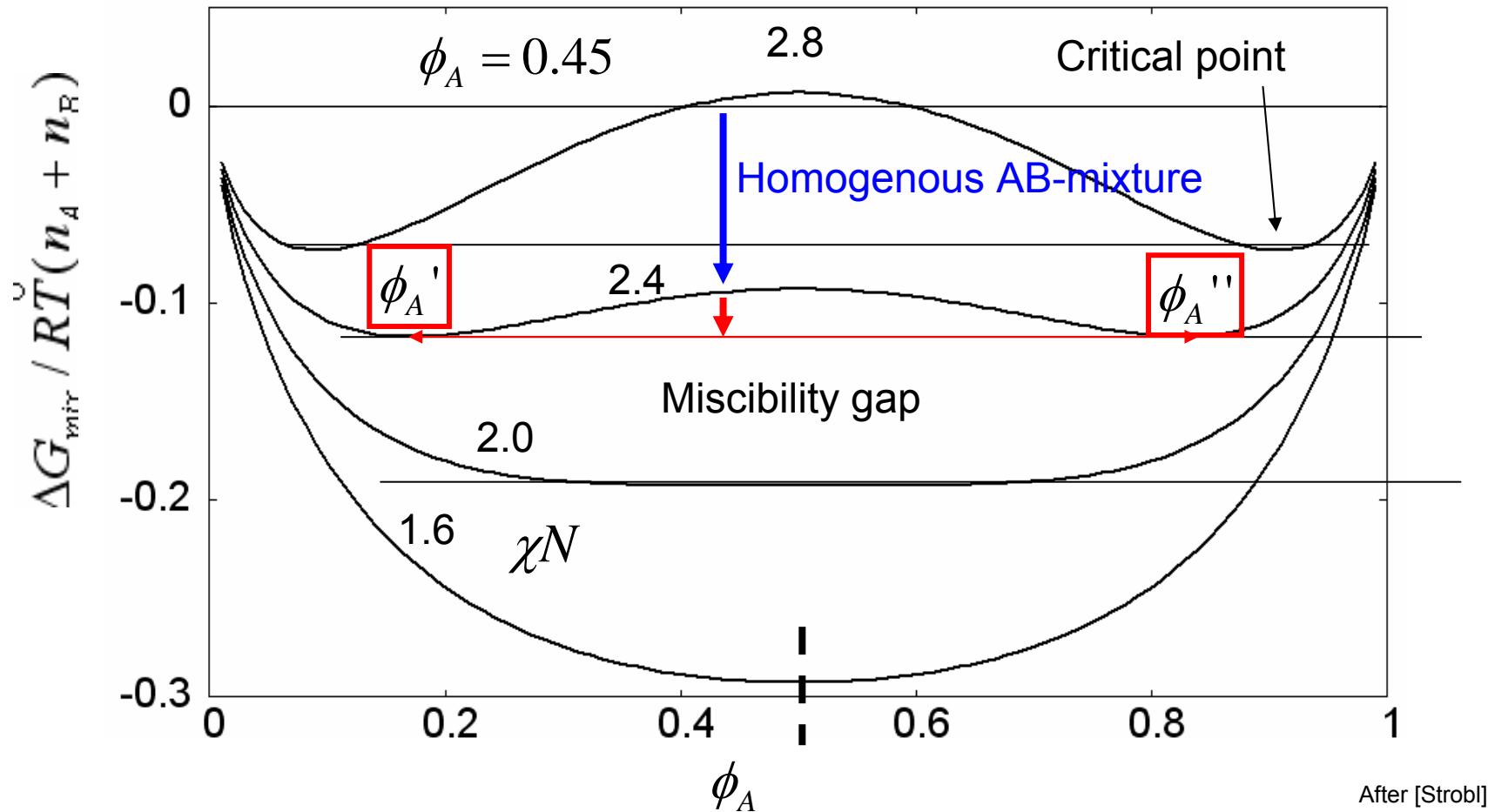
After [Strobl]

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

Phase diagrams

Consequences

$$\left.\frac{\partial^2 \Delta G_{mix}}{\partial \phi_A^2}\right|_{\phi_A=0.5} = \frac{1}{\phi_A} + \frac{1}{1-\phi_A} - 2\chi N = 0 \qquad \text{Vanishing curvature}$$

$$\chi N = 2 \qquad \text{Critical value: separates region with miscibility gap}$$

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

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

Critical concentrations

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

χN

Universal!

ϕ_A

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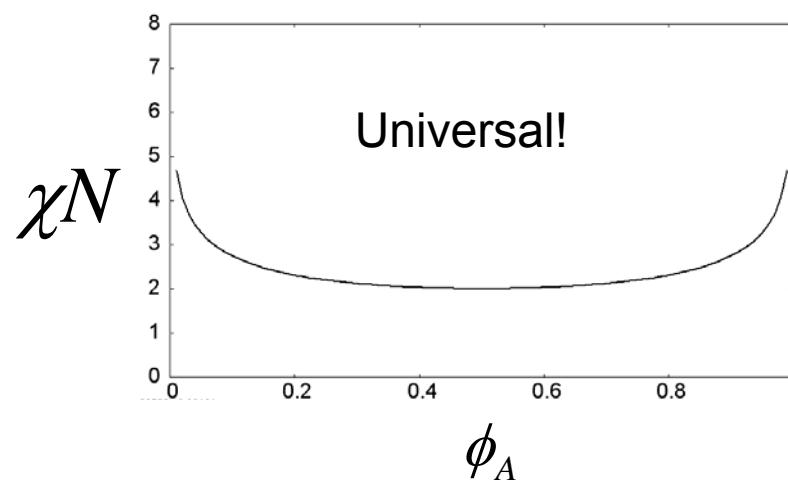
Phase diagrams

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…
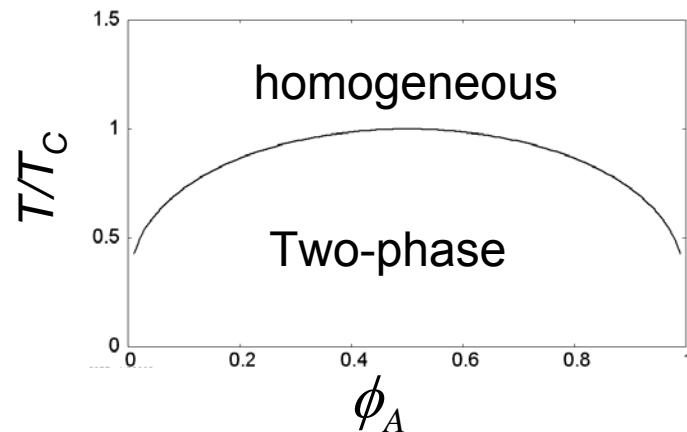
Partial crystalline polymers

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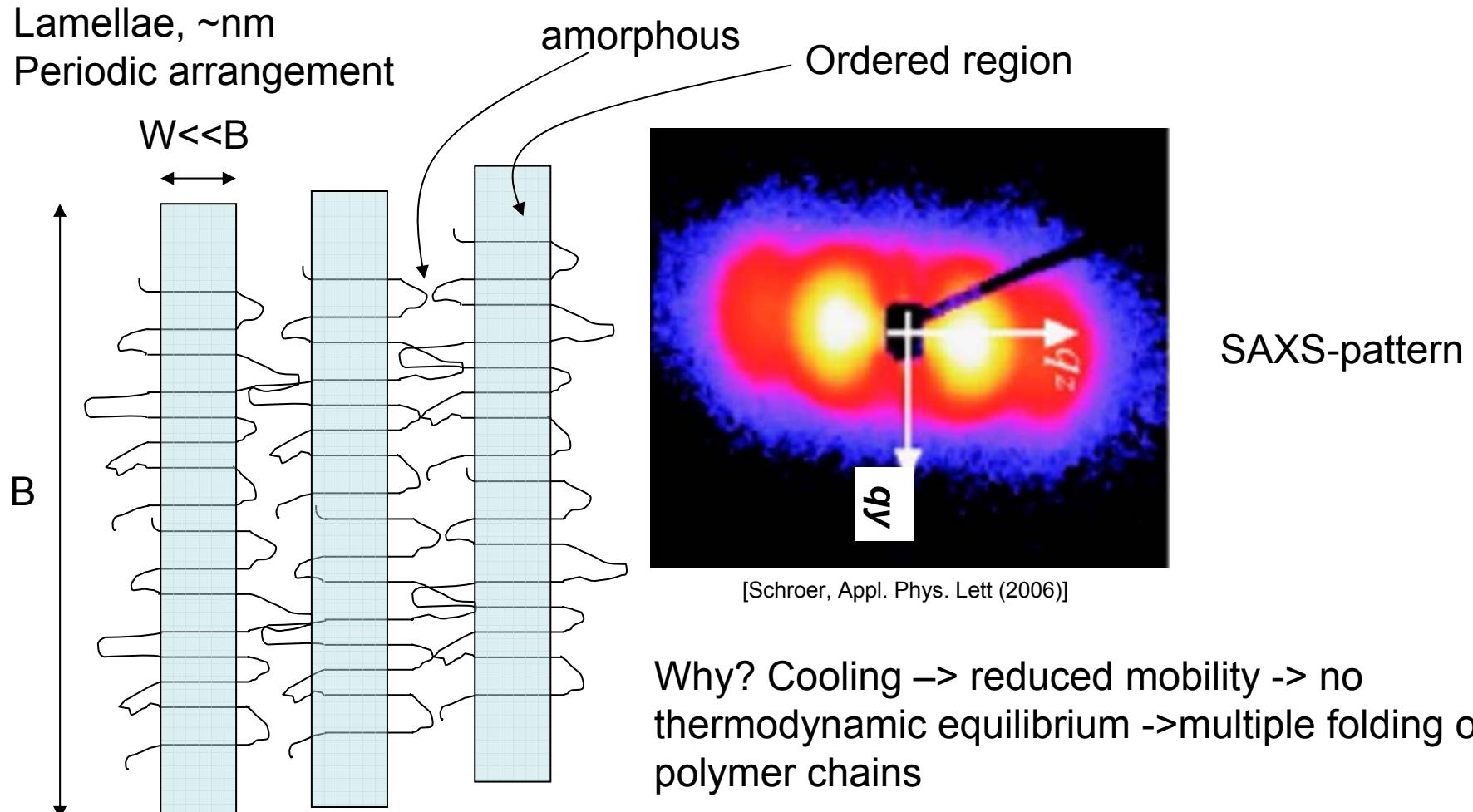
Why? Cooling –> reduced mobility -> no thermodynamic equilibrium ->multiple folding of polymer chains

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

…. AAAAABBBBBAAAAABBBBB…

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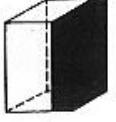
0.17   0.28   0.34   0.62   0.66   0.77   PS-b-PI
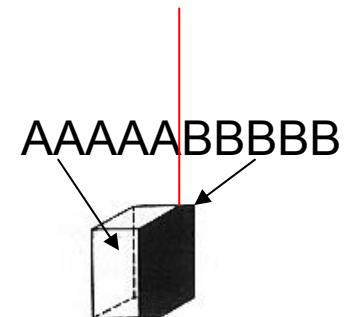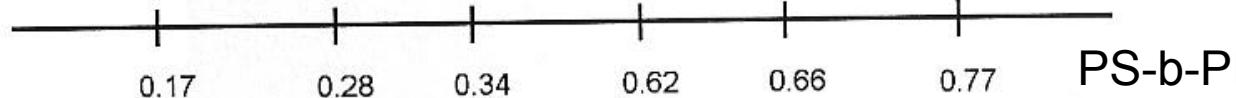
→ this is already a nanocomposite

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

Colloids

- Small particles, dispersed in liquid phase
- Polymers
- Metals
- 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
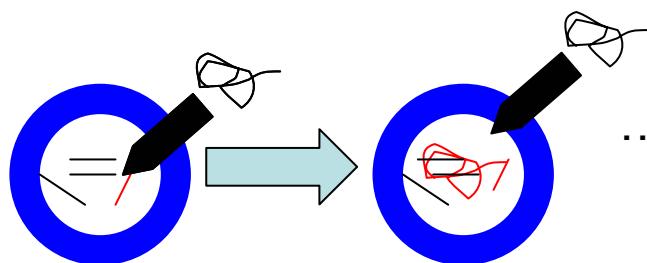
…until all monomer consumed:

32

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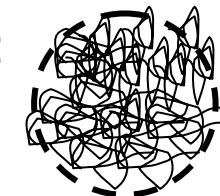
Colloids

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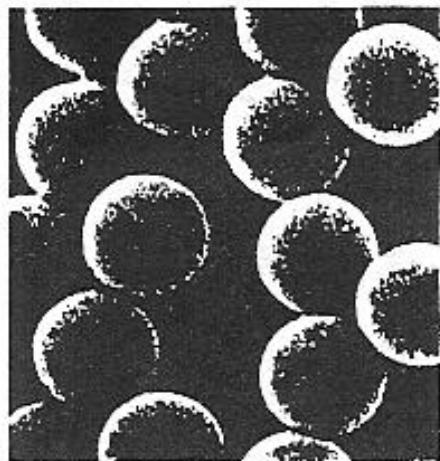
[Springer]
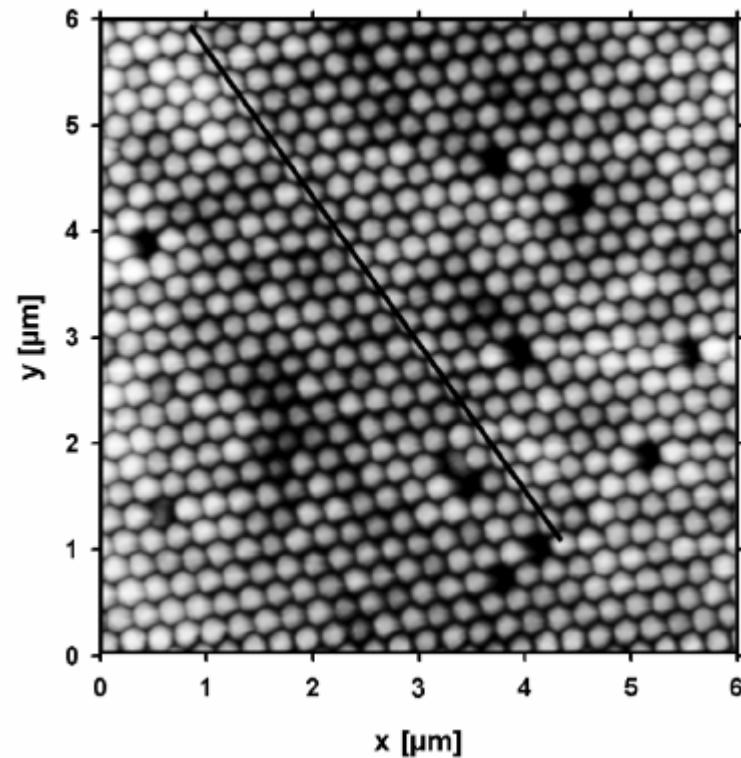
[Frömsdorf, J. Chem. Phys. (2006)]

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Application

Optical properties: sharp resonances $\Longleftrightarrow$ plasmon resonances
(visible light)　　　　cluster arrangement & shape
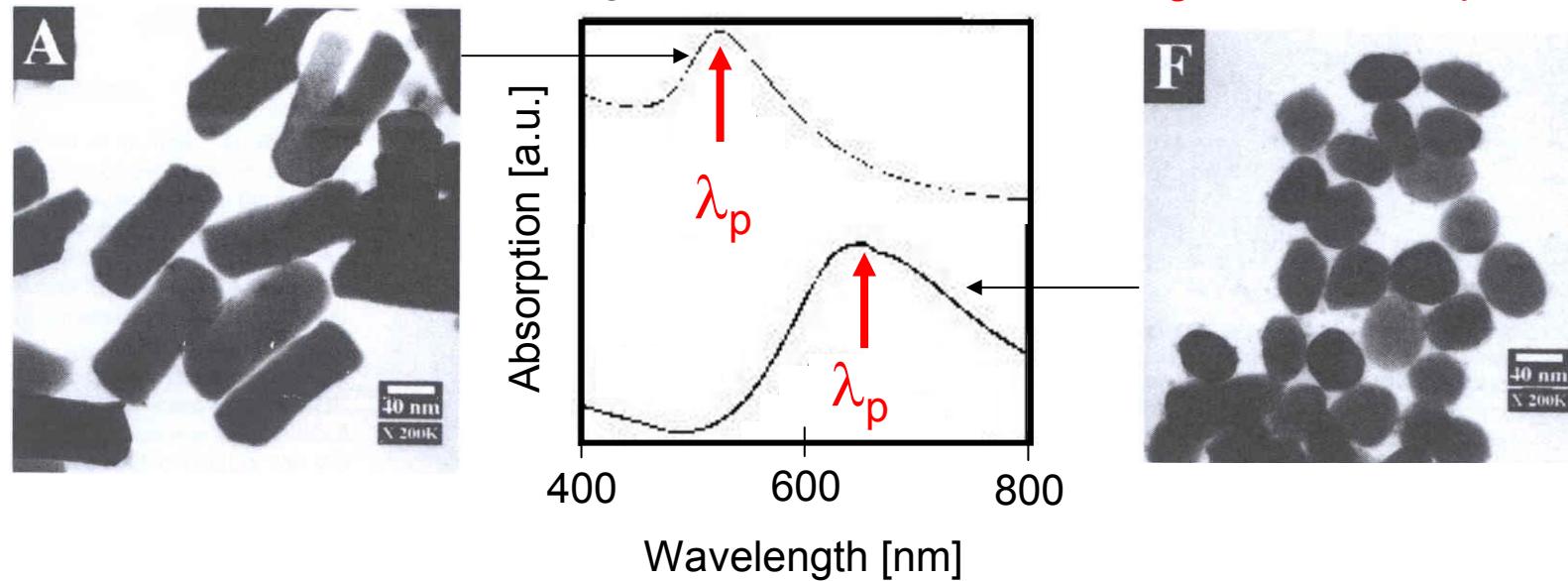
J.C. Hulteen et al., J Phys. Chem. B 101, 7727 (1997)

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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
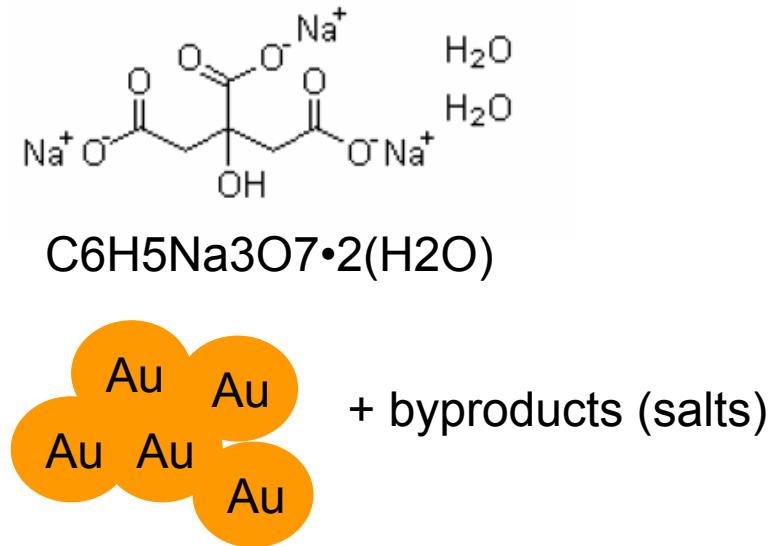
More structures: Core-Shell:

[Abul Kashem, Macromolecules (2008)]

Polymer-Metal Nanocomposites
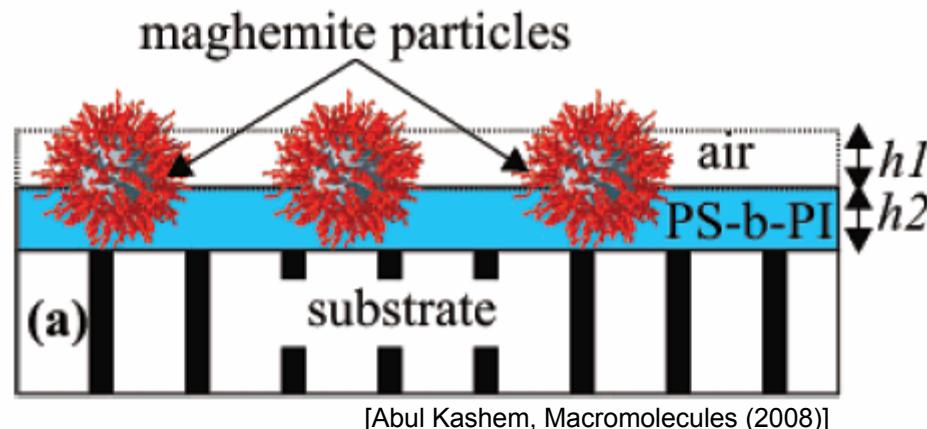
Biswas et al., Vac. Tech. Coat. **7**, 54 (2006).
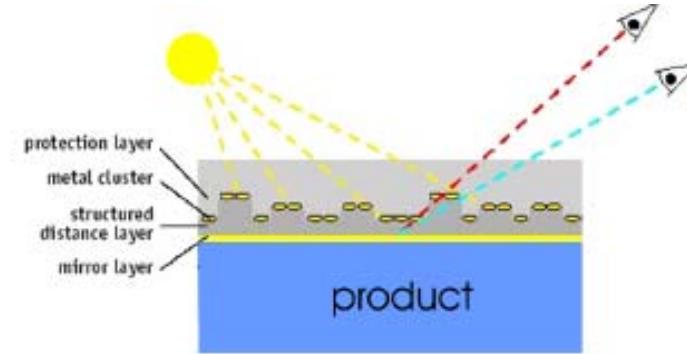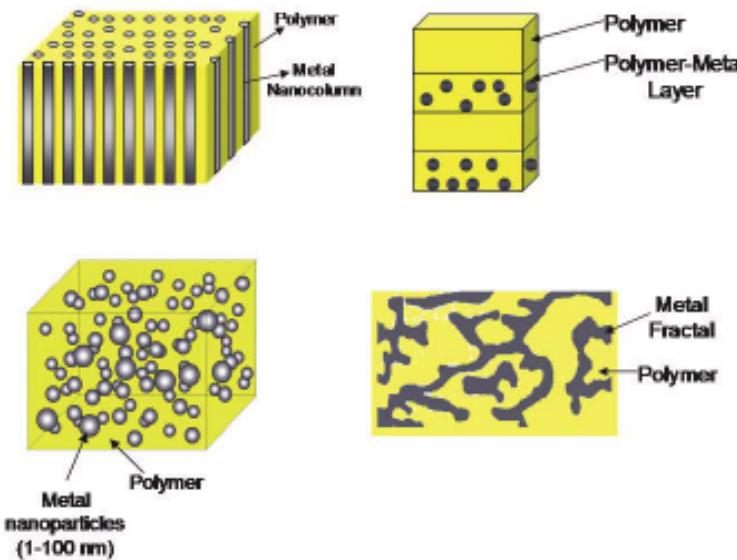

Bauer et al., Nanotechnology 14,1289 (2003)

http://www.siliconsolar.com

14°   90°
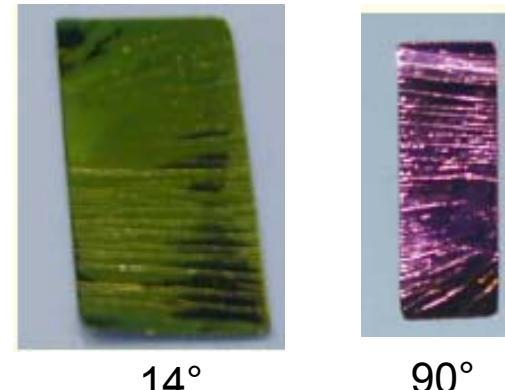
High-frequency filters
Solar cells

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

Anti-counterfeiting
Biosensors

Polymer-Metal Nanocomposites: Production

Sputter deposition:

Ar^+

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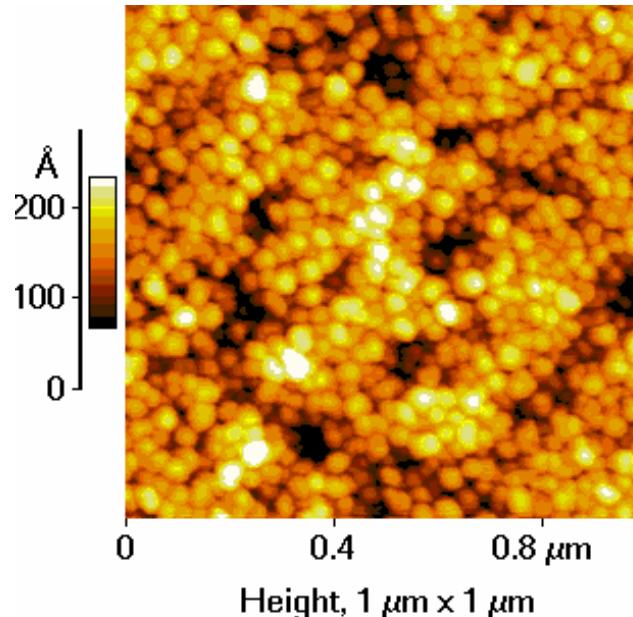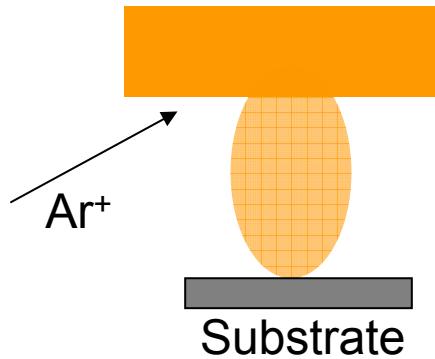
- Nice clusters, too
- Fast deposition method
- Usually broader size distribution
- self-assembly: Au-Au interaction much stronger than Au-Polymer interaction

Å
200
100
0

0   0.4   0.8 μm

Height, 1 μm x 1 μm

300nm

Noble metal (Au, Ag, Cu,…)
Polymer film
Substrate (Si, glass, + TiO2)
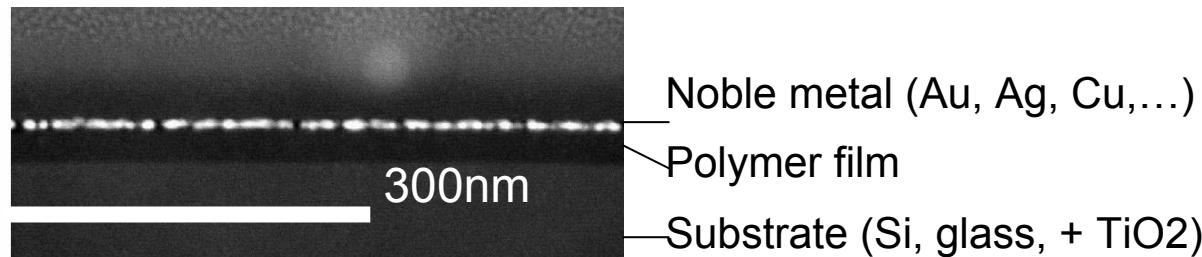
Roth et al., Appl. Phys. Lett. **88**, 021910 (2006)

Polymer-Metal Nanocomposites: Production

Sputter deposition:

Ar$^+$

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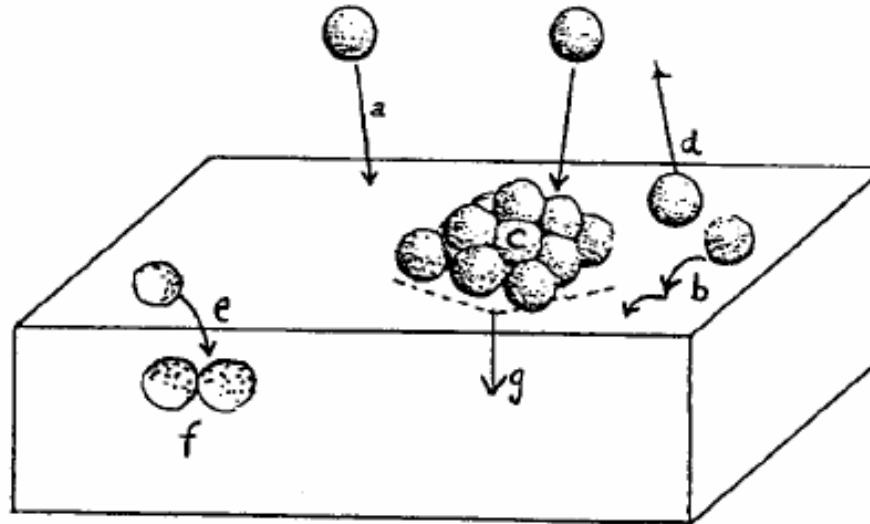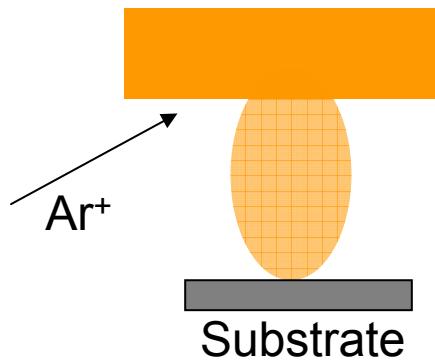
F. Faupel et al., in: Low Dielectric Constant Materials for IC
Applications, P. S. Ho, W. W. Lee, and J. Leu (Eds.), Springer
Verlag, 221 (2003) pp. 221

- Nucleation   - Growth   - Coalescence

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