Imperial College London

# Neutrons in soft matter

## Lecture 1 - Structure

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13th Oxford School on Neutron Scattering, 12-13 September 2013

# Outline

## Lecture 1 – Structure & kinetics – SANS

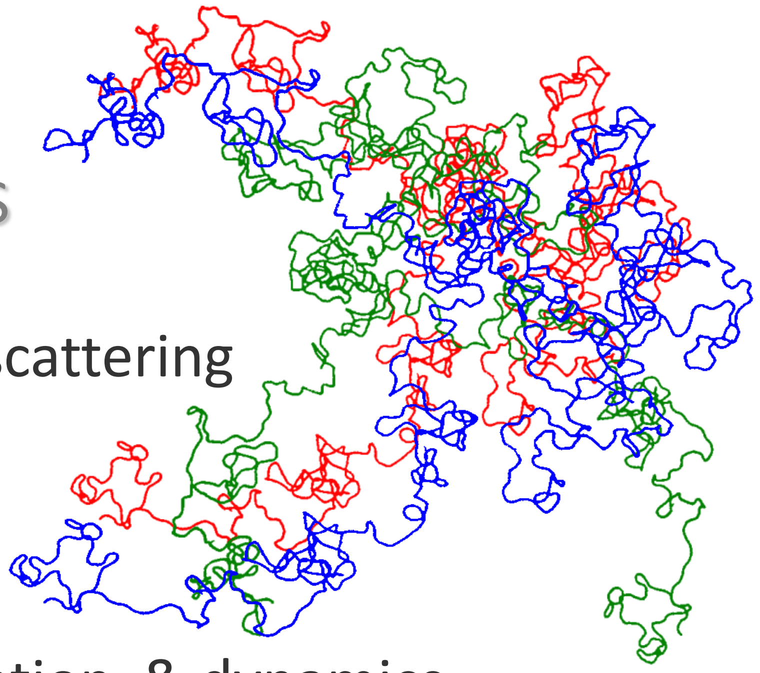
Introduction

soft matter & relevance of neutron scattering

Single objects: spheres, coils, rods...

Single chain polymer conformation
(solution and blends)

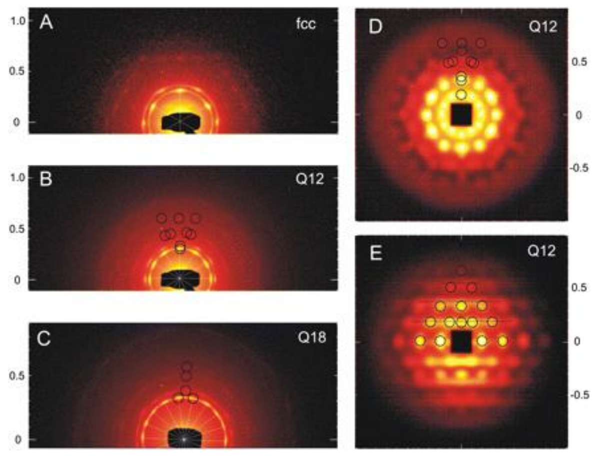
Polymer blends: interactions, conformation & dynamics
(equilibrium and phase separation)



## Lecture 2 – Interfaces and dynamics

Reflectivity and diffusion

Dynamics in soft matter, QENS, BS, Spin-echo




Forster et al (2011)

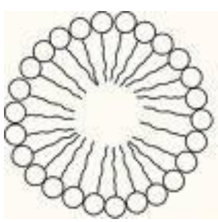
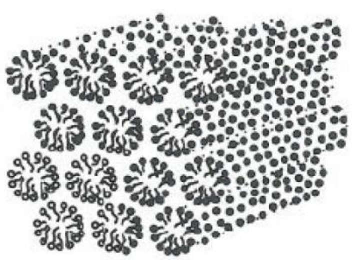
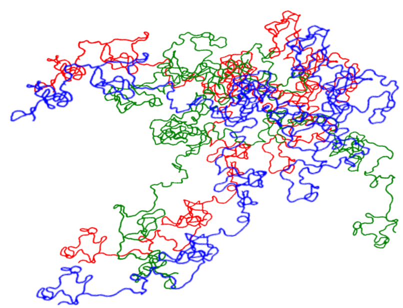
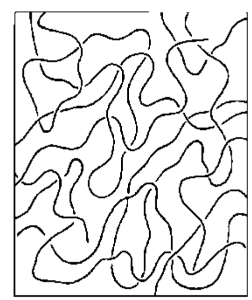
# Soft Matter

**"molecular systems giving a strong response to very weak command signal"**

**deGennes (1991)**

Condensed matter: states are easily deformed by small external fields, including thermal stresses and thermal fluctuations.

Relevant energy scale comparable with room temperature thermal energy.

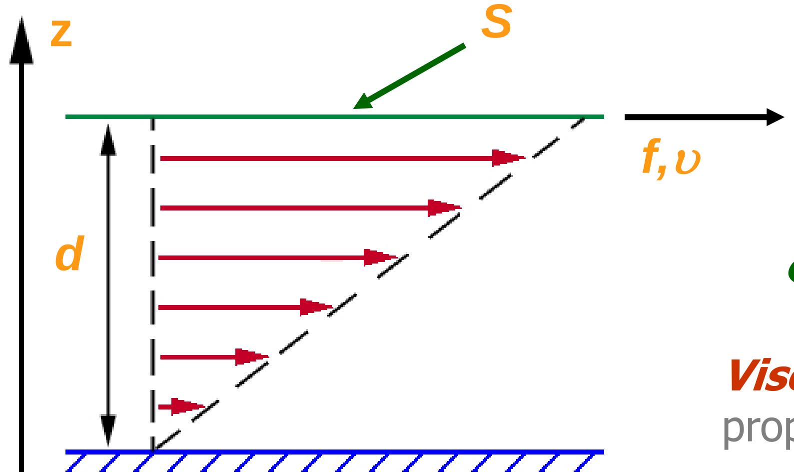
Complex fluids: including colloids, polymers, surfactants, foams, gels, liquid crystals, granular and biological materials.

**shear**

**Movie: complex fluids are generally non-Newtonian... and structured**

# Viscosity

Simplest setup to measure viscosity

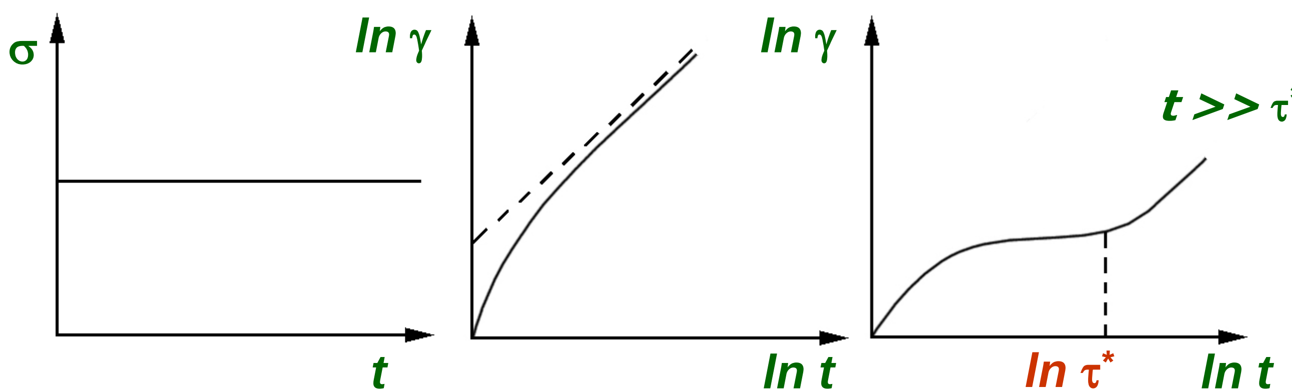



$$f = \eta \frac{S\upsilon}{d}$$

$$\sigma = \frac{f}{S} = \eta \frac{d\upsilon}{dz}$$

***Viscosity:***
proportionality coefficient $\eta$

# Viscoelasticity?




Step-wise stress starting at *t* =0

normal liquid

polymer

$t << \tau^*$ : *elastic* response

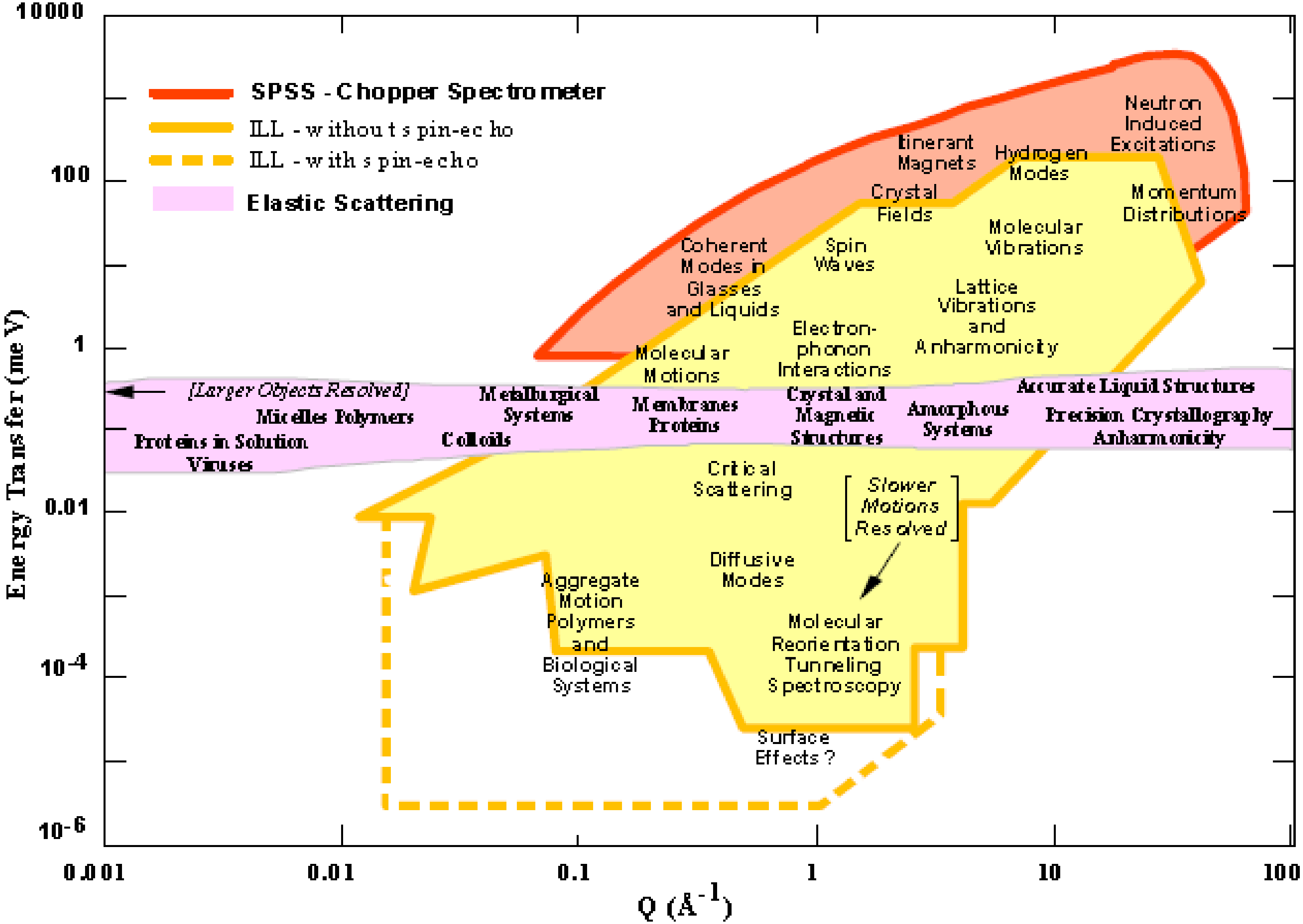
$$\gamma \approx \sigma / E$$

$t >> \tau^*$ : *viscous* response

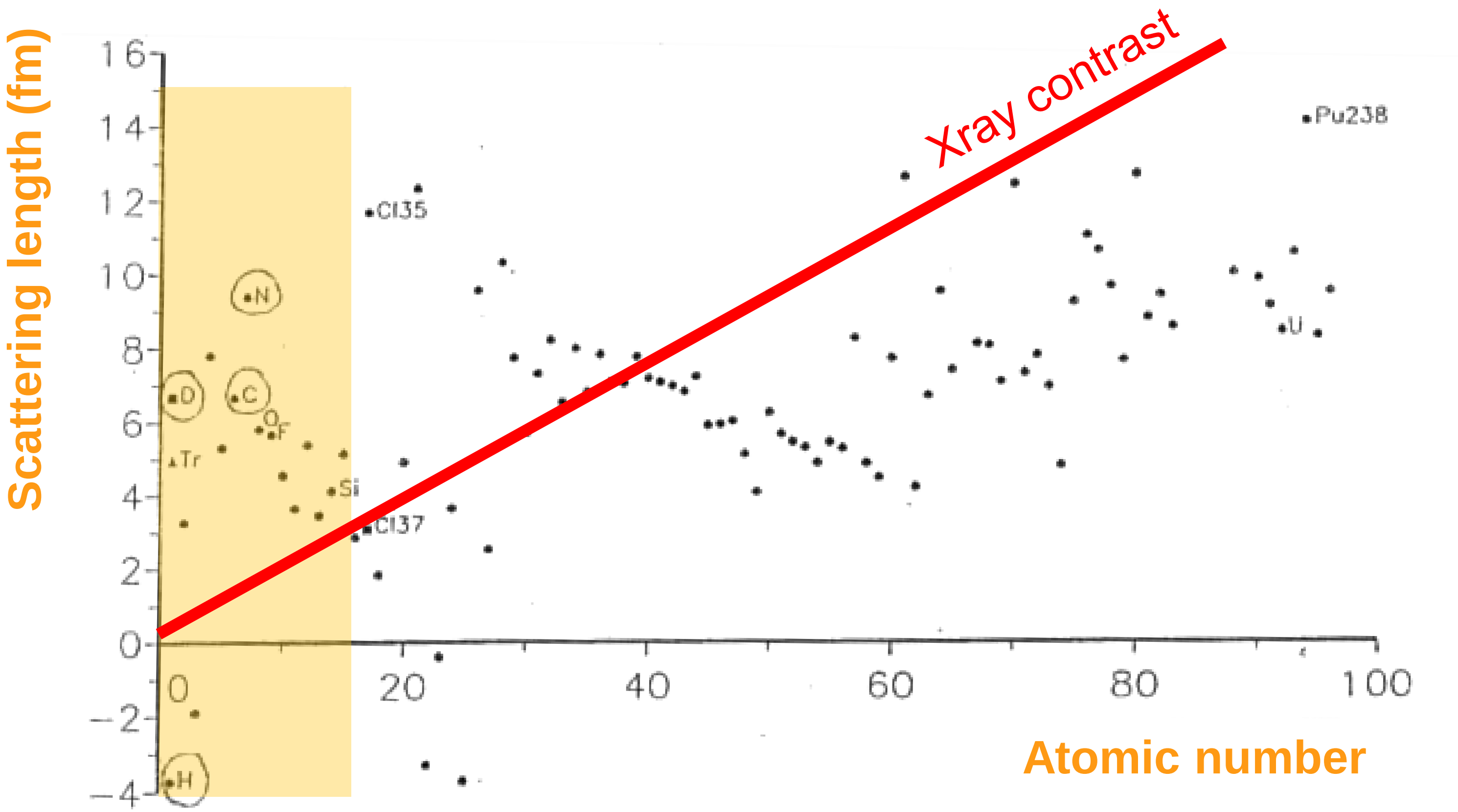
$$\gamma \propto \sigma \cdot t / \eta$$

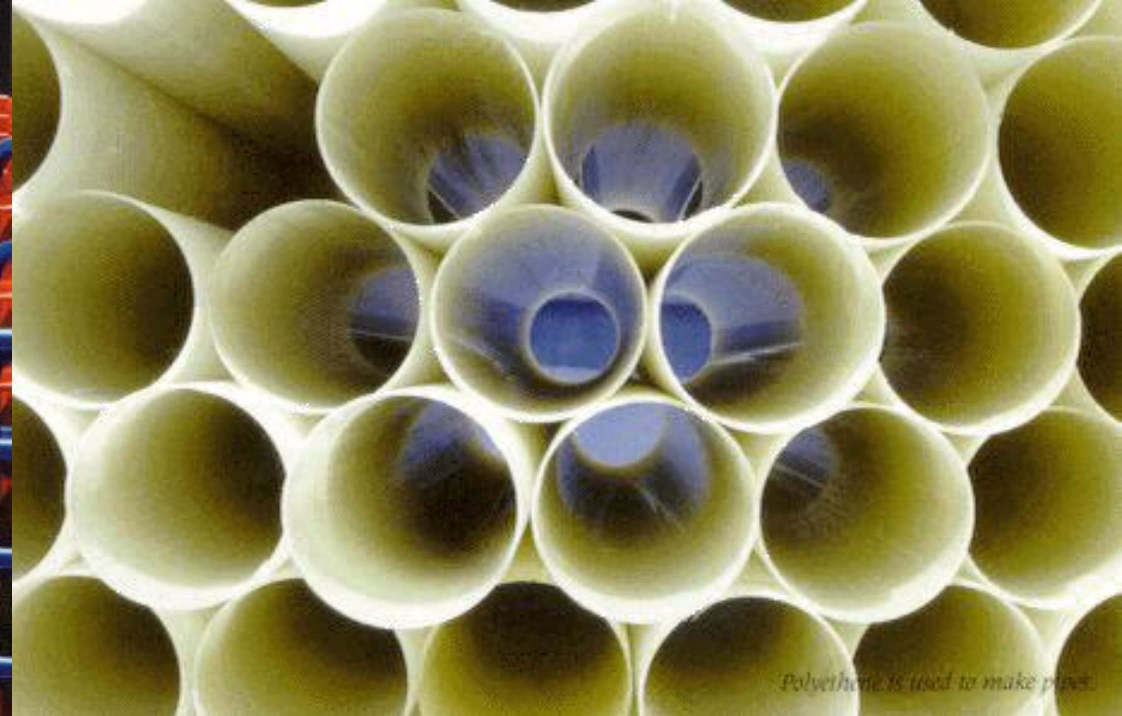
γ **shear angle**

# Neutron scattering is *key* in soft condensed matter



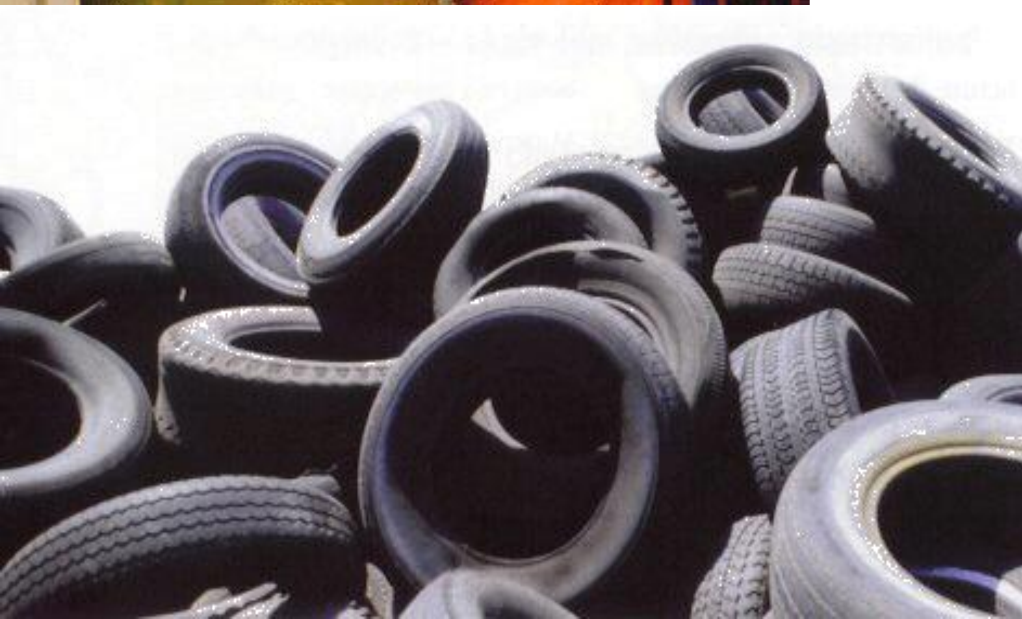
# Neutron scattering is *key* in soft condensed matter



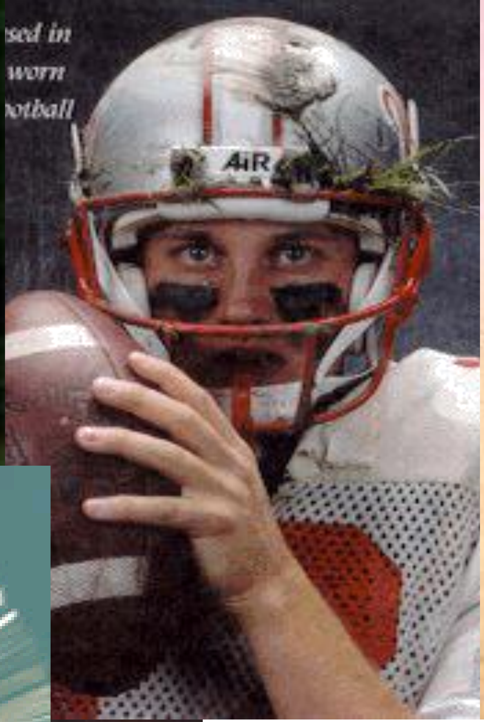


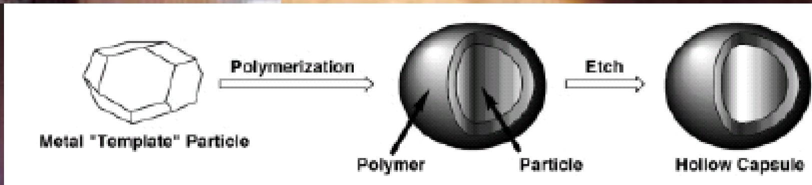
Polyethene is used to make pipes.

# Common soft matter

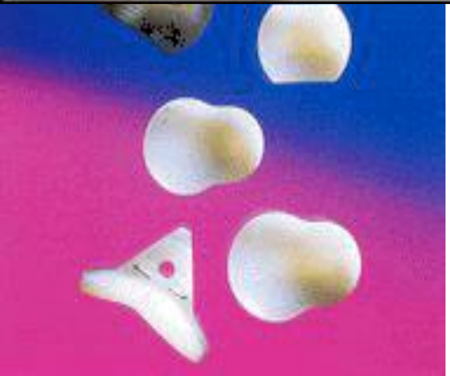



Household products packaged in plastic containers.
Courtesy of British Plastics Federation.





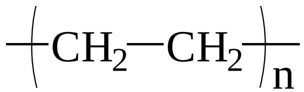




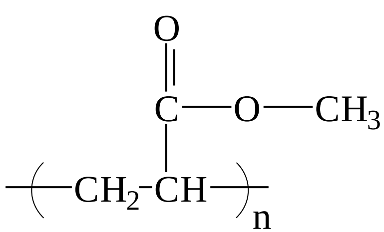
# Speciality polymers

# Common polymers

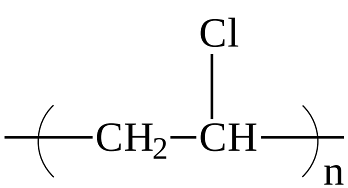
PE poly(ethylene)



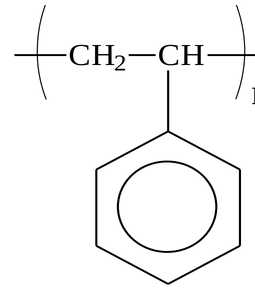

PMMA poly(methylmethacrylate)



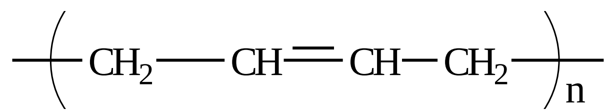

PVC poly(vinylchloride)



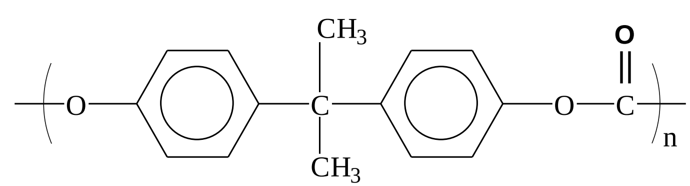

PS poly(styrene)




PB poly(butadiene)

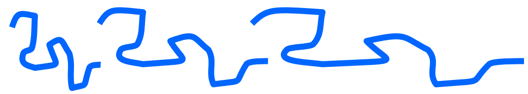



BPA-PC bisphenol-A polycarbonate

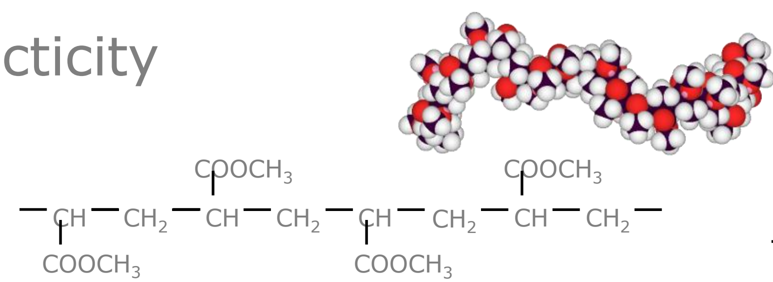


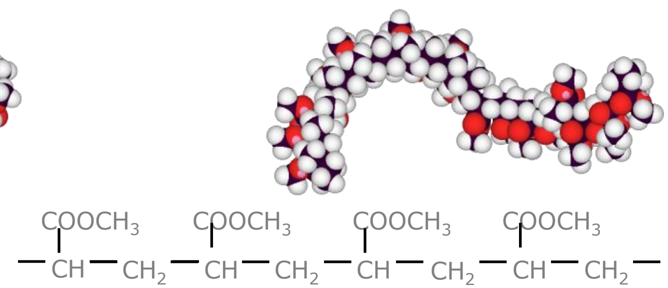
# Polymer key properties

Molecular weight, N  (size)

Polydispersity  (distribution of sizes)

Tacticity



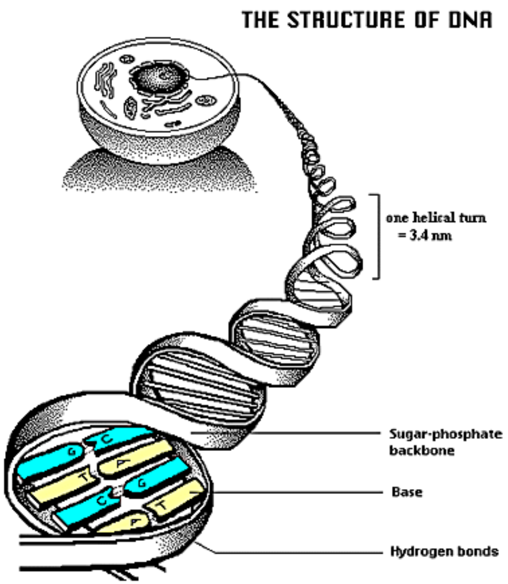


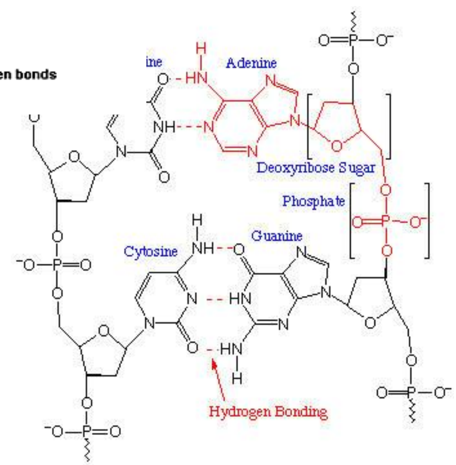
Glass transition (solid-liquid)

Crystallinity

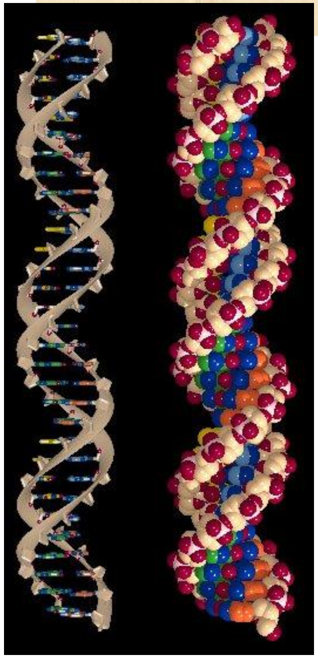
Interaction parameter $\chi$ $\longrightarrow$ Combine properties to make new materials!

# Soft matter: DNA

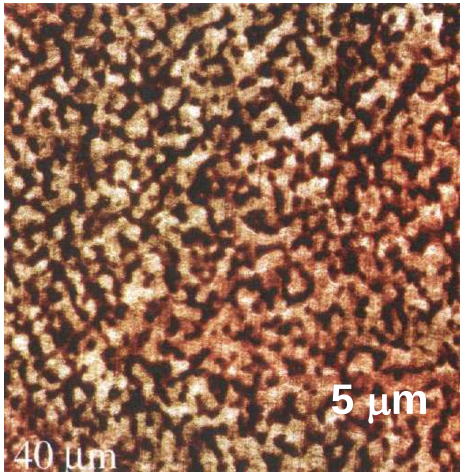


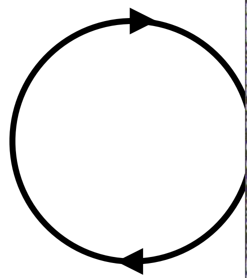


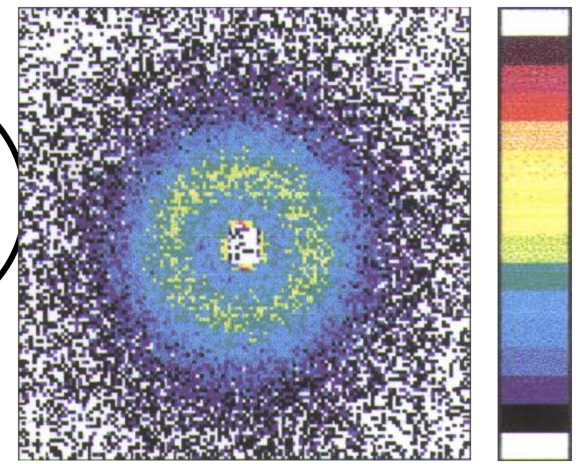


# Soft Matter: membranes, photovoltaics (BHJ)

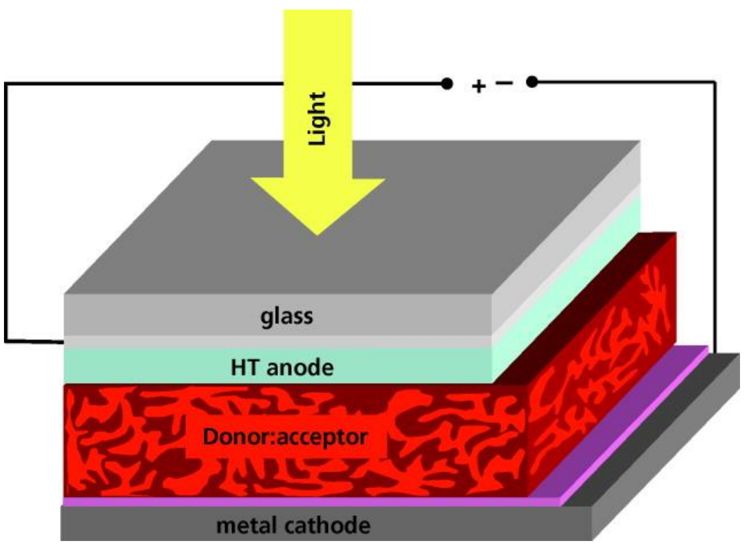



Real space

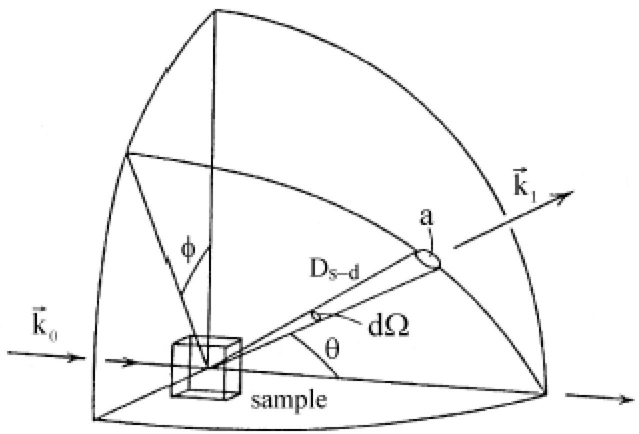




Reciprocal space



# Scattering theory reminder




## Scattering cross section

$$\frac{d^2\sigma}{d\Omega dE} = \left(\frac{d^2\sigma}{d\Omega dE}\right)_{coh} + \left(\frac{d^2\sigma}{d\Omega dE}\right)_{inc}$$

*coherent* *incoherent*

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{coh} = \frac{1}{2\pi\hbar}\frac{k_1}{k_0}\frac{\sigma_{coh}}{4\pi}\int_{-\infty}^{+\infty}\sum_{i,j}\left\langle e^{-i\mathbf{q}\cdot\mathbf{R}_i(0)}e^{i\mathbf{q}\cdot\mathbf{R}_j(t)}\right\rangle e^{-i\omega t}dt$$

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)_{inc} = \frac{1}{2\pi\hbar}\frac{k_1}{k_0}\frac{\sigma_{inc}}{4\pi}\int_{-\infty}^{+\infty}\sum_{i}\left\langle e^{-i\mathbf{q}\cdot\mathbf{R}_i(0)}e^{i\mathbf{q}\cdot\mathbf{R}_i(t)}\right\rangle e^{-i\omega t}dt$$

## Dynamic structure factor

**FT (*t*, *ω*)**

$$S(\mathbf{q},\omega) = \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} I(\mathbf{q},t)e^{-i\omega t}dt.$$

$\int d\omega$

## Elastic structure factor

$$\int_{-\infty}^{+\infty} S(\mathbf{q},\omega)|_{\mathbf{q}=Const.}\, d\omega = S(\mathbf{q})$$

## Intermediate scattering function

**FT (*r*, *q*)**

$$I_s(\mathbf{q},t) = \frac{1}{N}\sum_i\left\langle e^{-i\mathbf{q}\cdot\mathbf{R}_i(0)}e^{i\mathbf{q}\cdot\mathbf{R}_i(t)}\right\rangle e^{-i\omega t}.$$

## Pair correlation function

$$G(\mathbf{r},t) = \frac{1}{(2\pi)^3}\int I(\mathbf{q},t)e^{-i\mathbf{q}\cdot\mathbf{r}}d\mathbf{q}.$$

**S(q)**

$$S(q) = Nz^2P(q) + N^2z^2Q(q)$$

Form factor

$$P(q) = \frac{1}{z^2}\sum_{i=1}^{z}\sum_{j=1}^{z}\langle e^{-i\mathbf{q}\cdot\mathbf{r}_{ij}}\rangle$$

Structure factor

$$Q(q) = \frac{1}{z^2}\sum_{i_p=1}^{z}\sum_{j_q=1}^{z}\langle e^{-i\mathbf{q}\cdot\mathbf{r}_{i_p j_q}}\rangle$$

# Reminder: Fourier Transforms

$$H(f) = \int_{-\infty}^{\infty} h(t)\, e^{2\pi i f t}\, dt$$

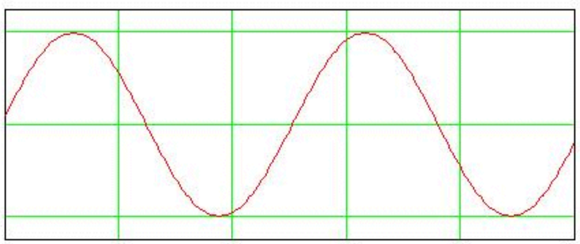
$$h(t) = \int_{-\infty} H(t)\, e^{-2\pi i f t}\, df$$

Fourier transform:

$\Phi(H(f),t) = h(t)$

$\Phi^{-1}(h(t),f) = H(f)$

h(t)

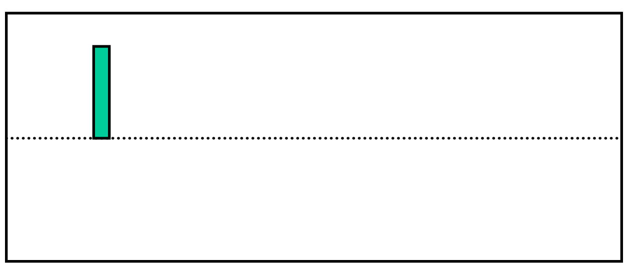


t

$$h(t) = Ae^{i(t+\phi)}$$

$$H(f) = \int_{-\infty}^{\infty} h(t)\, e^{2\pi i f t}\, dt$$

H(f)



f

$H(f) = 0 \qquad \text{if } (ft \neq 1)$

$H(f) = A\, e^{i\phi} \qquad \text{if } (ft = 1)$

# Reminder: Fourier Transforms

$$H(f) = \int_{-\infty}^{\infty} h(t)\, e^{2\pi i f t}\, dt$$

$$h(t) = \int_{-\infty} H(t)\, e^{-2\pi i f t}\, df$$

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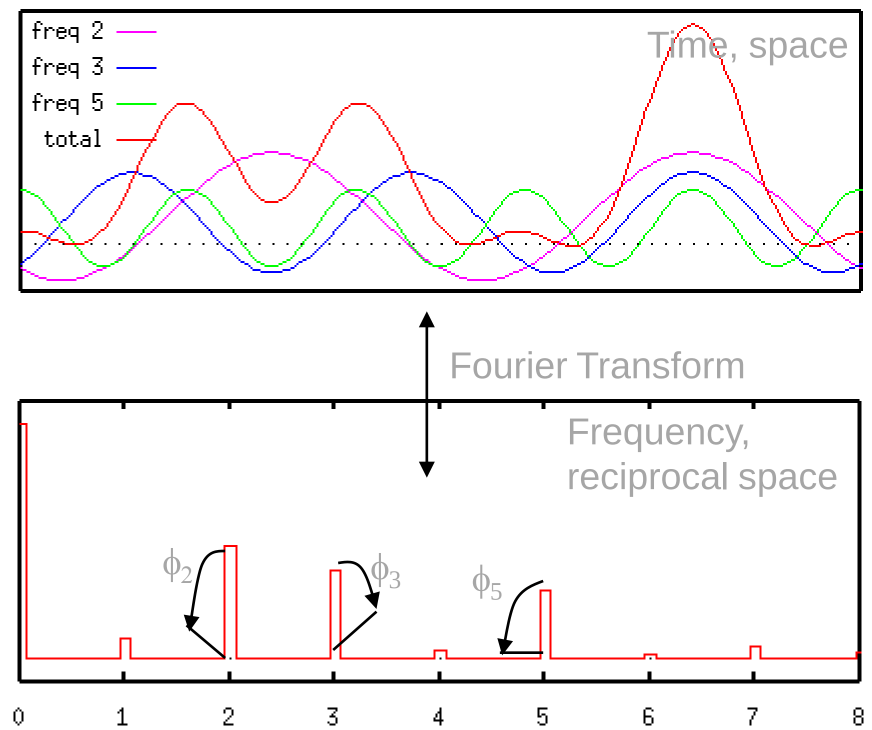
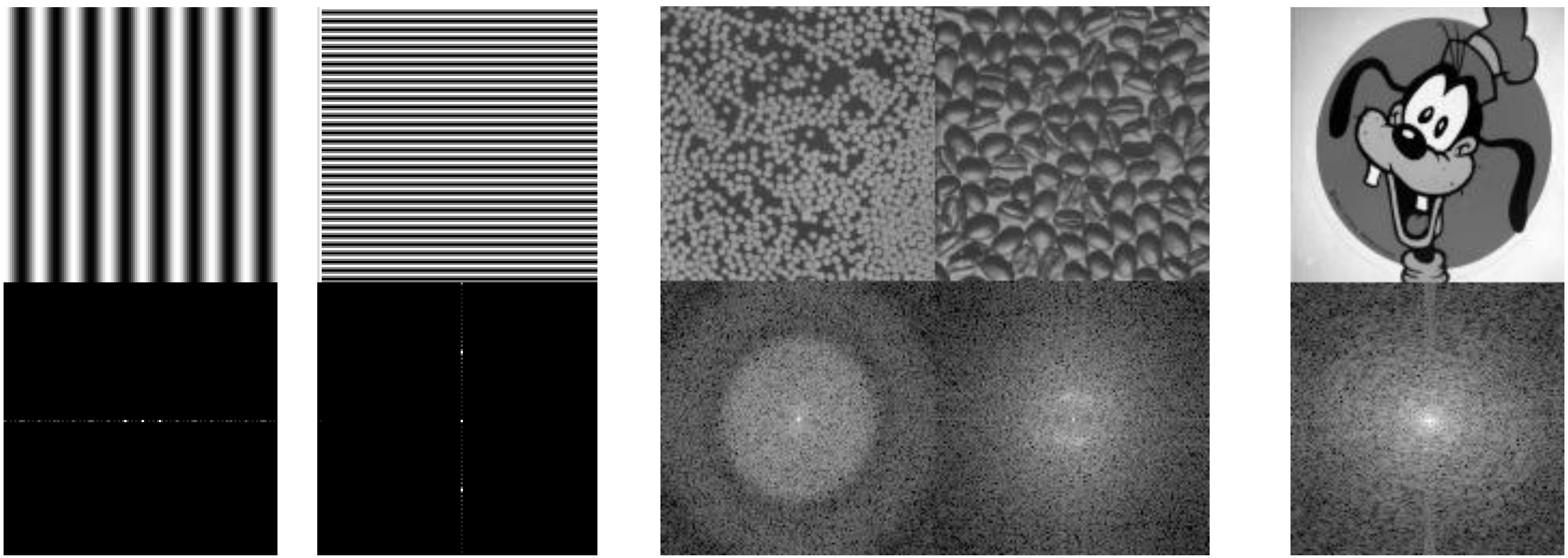


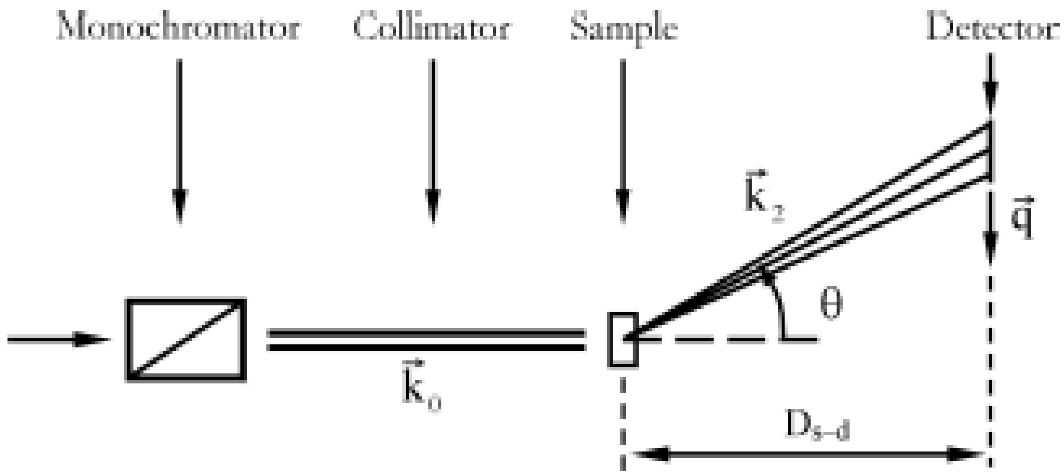
# Reminder: Fourier Transforms

Real space



Reciprocal space

# SMALL-ANGLE NEUTRON SCATTERING




$$q = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

$$q \approx \frac{2\pi}{\lambda}\theta$$

$$q \approx \frac{2\pi}{\lambda}\frac{R}{D_{s-d}}$$

Absolute scattering intensity [cm$^{-1}$]

$$\frac{\partial\sigma}{\partial\Omega}(Q) = N_p\, V_p^2\, (\Delta\delta)^2\, P(Q)\, S(Q) + B_{inc}$$

incoherent background

structure factor

volume

number density

form factor

contrast

Scattering length density

$$\delta = \sum_i b_i \cdot \frac{D\, N_A}{M_w}$$

# Relationship between *q λ θ* and *d*

$$\boxed{q = \frac{4\pi}{\lambda}\sin(\theta/2)}$$

$$\boxed{d = \frac{2\pi}{q}}$$

small q ~ large d [large q ~ small d]

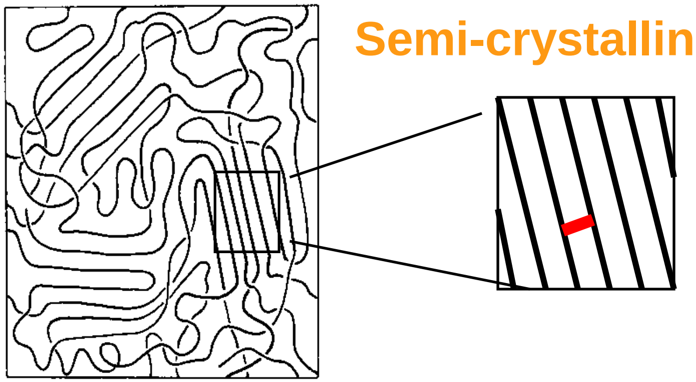
small λ ~ large q ~ small d
[large λ ~ small q ~ large d]

| Radiation | Wavelength |
|---|---|
| light | ~ 500 nm |
| X-rays | ~ 1 Å |
| neutrons | ~ 5 Å |

Ångstrom:
1 Å = $10^{-10}$ m
1 nm = 10 Å

<u>Bottom line:</u>
radiation of small wavelength λ can 'see' smaller sample features d
(provided that contrast is sufficient).

# Example: crystalline structure of polymer



Semi-crystalline poly(ethylene) PE

lamella spacing is **d ~ 20 nm**

$q = 2\pi/d \sim 0.3\ nm^{-1}$

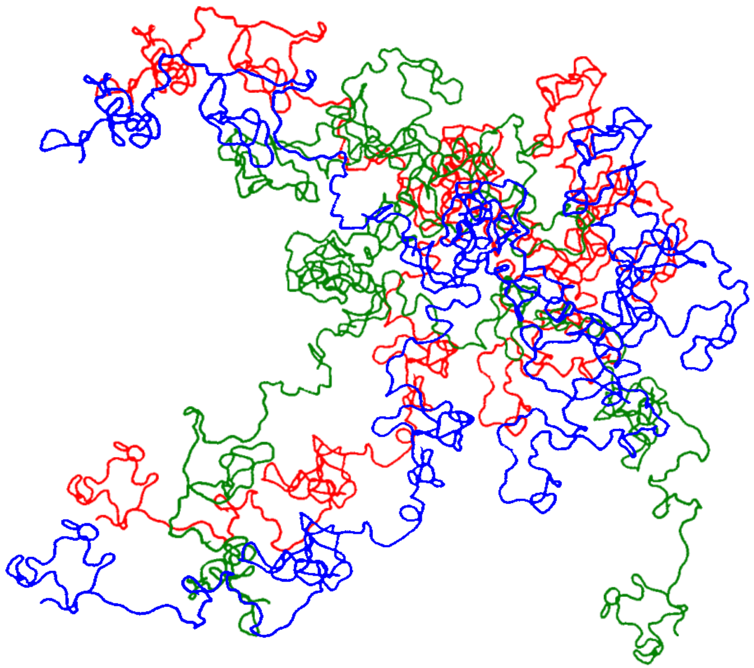
$$q = \frac{4\pi}{\lambda}\sin(\theta/2)$$

| Radiation | Wavelength | Scattering angle |
|---|---|---|
| X-rays | ~ 1 Å | θ ~ 0.27 degrees |
| neutrons | ~ 5 Å | sin(θ/2) ~ 0.013, θ ~ 0.7 degrees |
| light | ~ 500 nm | sin(θ/2) > 1 **impossible!** |

the smallest dimension probed by wavelength λ corresponds to largest angle θ=180 degrees (backscattering). For light $d_{min}$~ 0.25 μm, for X-rays or neutrons $d_{min}$~ 0.5 to 2.5 Å.

In typical experiments, scattering angles range from 0.1 < θ < 70 degrees

# A brief history of polymers



1920 Staudinger proposed plastics are long molecules with covalent bonds.

1940 Kuhn established they are usually flexible

1953 Flory described the shape and size of individual polymer molecules in solutions and melts.

1967 Edwards – polymer molecules in rubbers and glasses are trapped by neighbours in a “tube”. Chain confirmation ↔ trajectories quantum particles.

1971 de Gennes – molecules in tube move like snakes and eventually escape

# Main factors governing polymer physical properties :

**1. Number of monomer units in the chain, N is large $N >> 1$.**

**synthetic polymers** $N \approx 10^2 - 10^4$ **DNA** $N \approx 10^9 - 10^{10}$

**2. Monomer units are connected in the chain.** $\Rightarrow$ **no freedom of independent motion (unlike systems of disconnected particles, e.g. low molecular gases and liquids).** $\Rightarrow$ **Polymer systems are *poor in entropy*.**

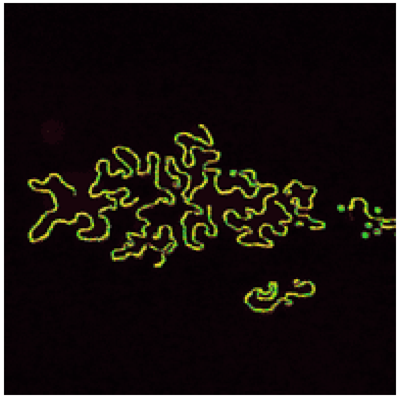
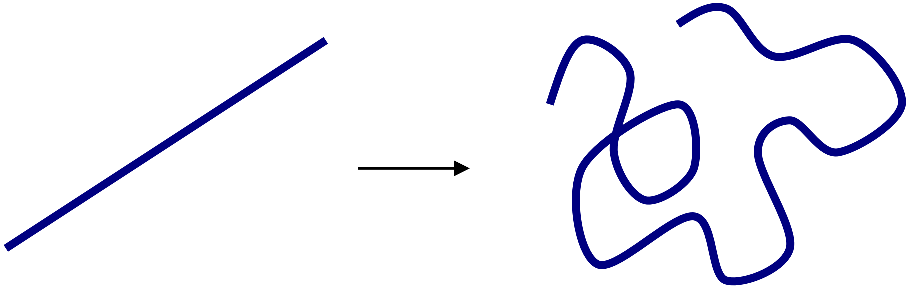


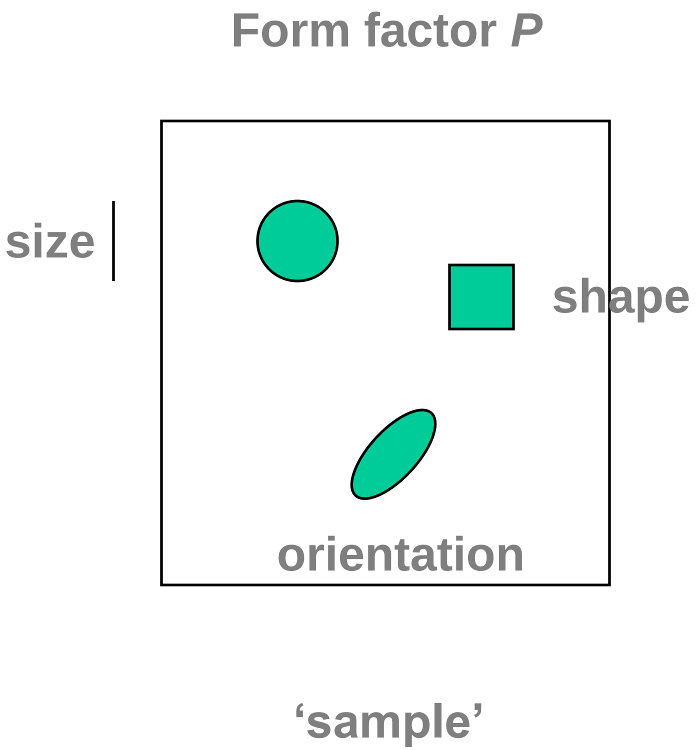
Image single molecule (AFM) Magonov

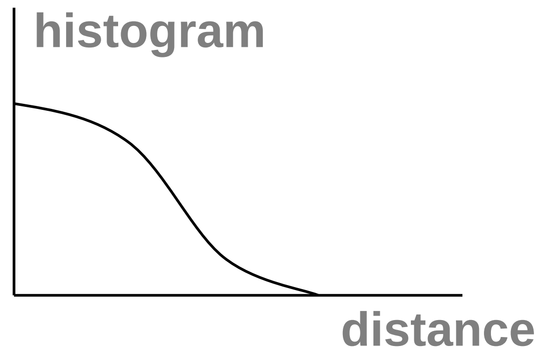
**3. Polymer chains are generally *flexible*.**



# Form factor: P

*Self-correlations*



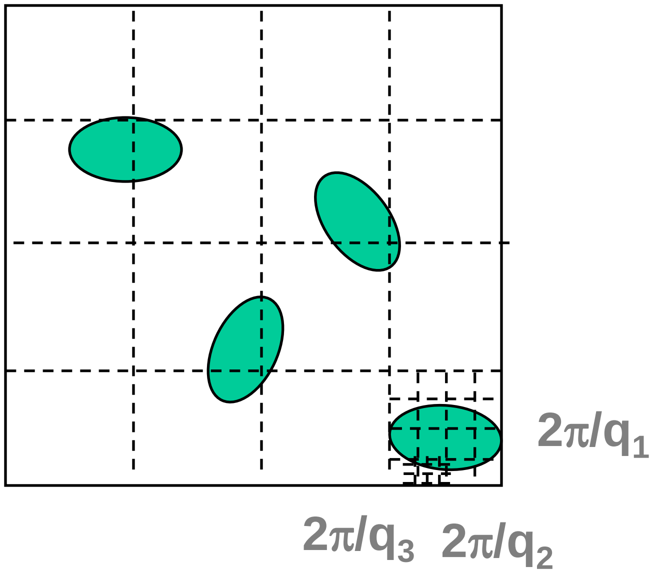



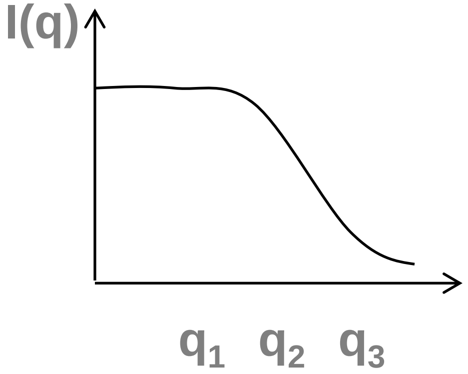

$$P(Q) = \frac{1}{V_p^2} \left| \int_0^{V_p} \exp\left[i\ f(Q\,\alpha)\right]\ dV_p \right|$$

Interference between scattered radiation from different parts of the same object

(analytical solutions for common shapes)

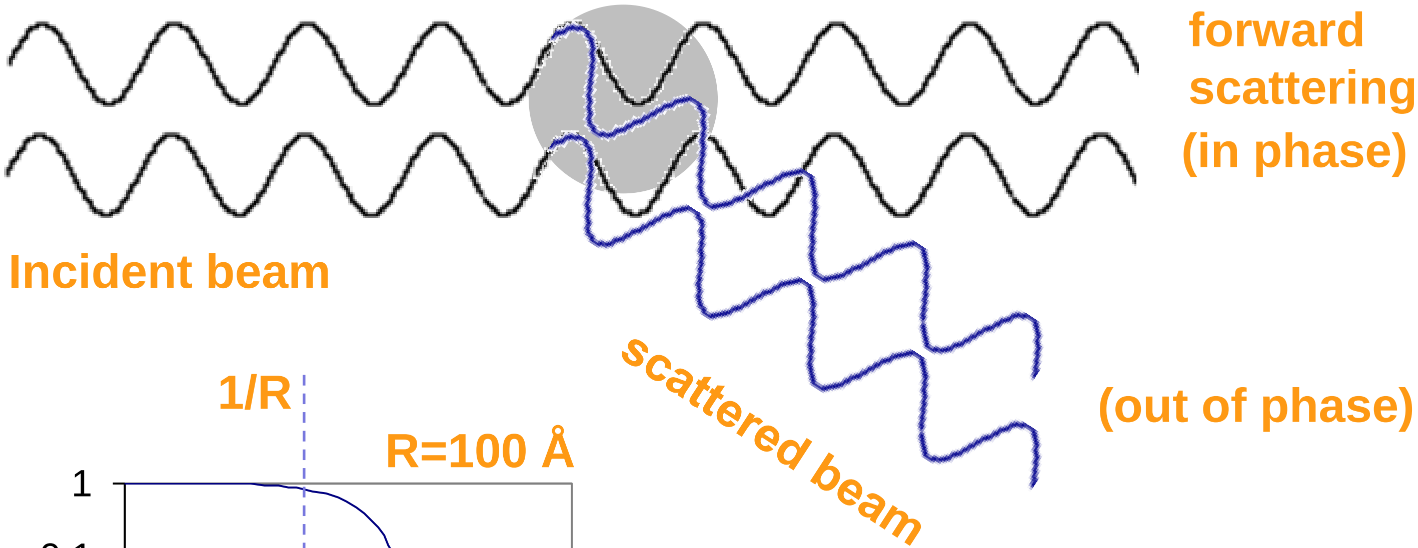
# Multiple lengthscales

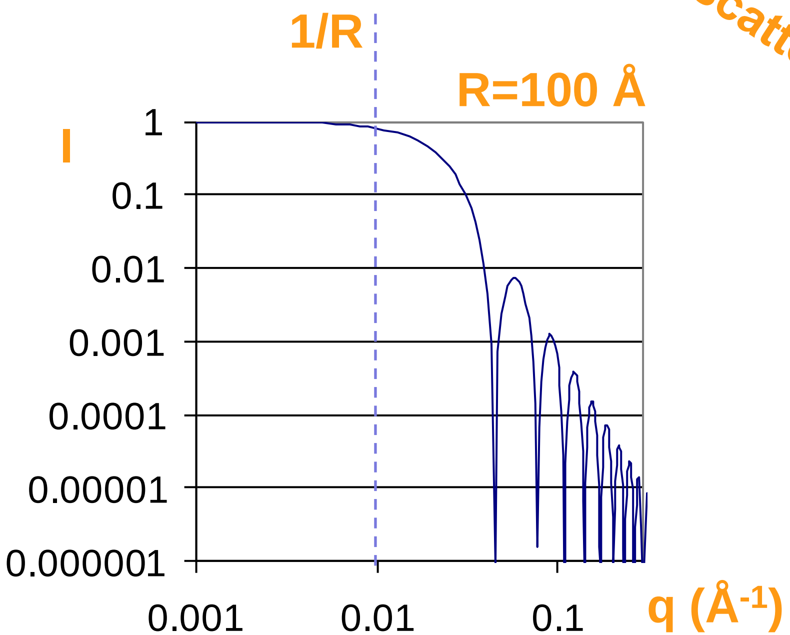



scattering spectrum corresponds to different “magnifications”, thus several approximations may be relevant

# Scattering from a sphere

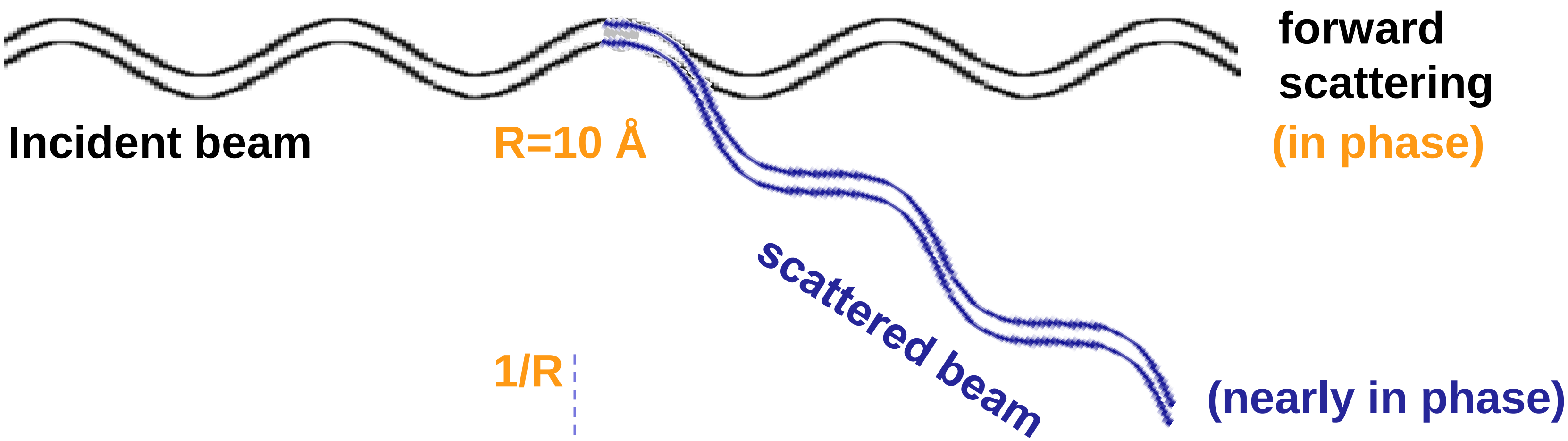


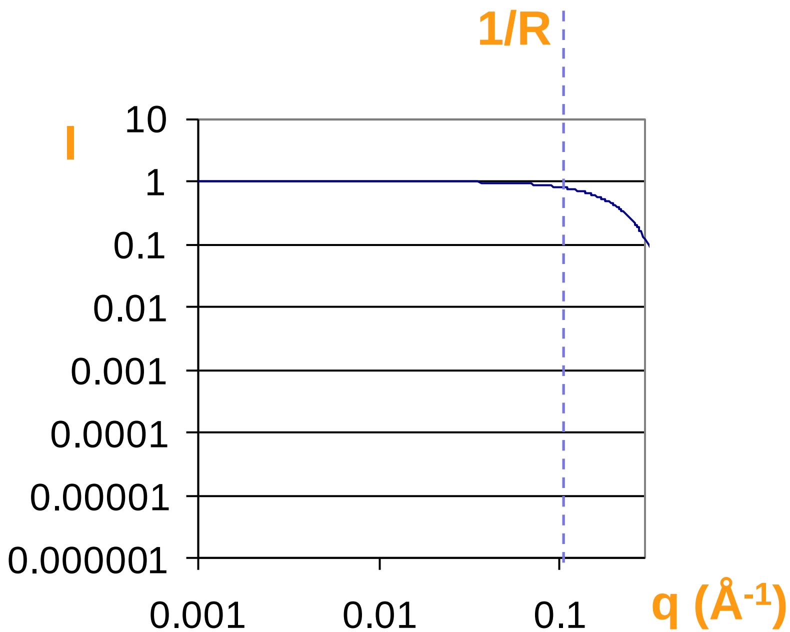




$$P(q) = \frac{9\left(\sin qR - qR\cos qR\right)^2}{\left(qR\right)^6}$$

$$R_g^2 = \frac{3}{5}r^2$$

# Scattering from a (tiny) sphere

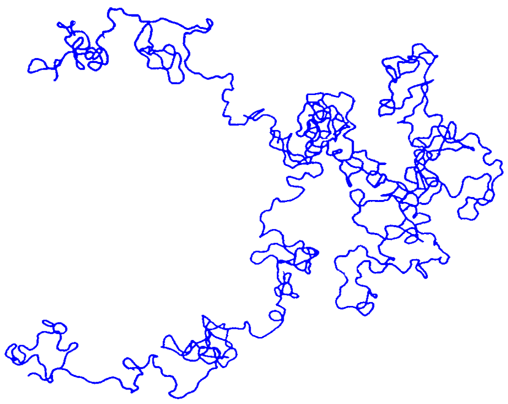



$$P(q) = \frac{9\left(\sin qR - qR\cos qR\right)^2}{\left(qR\right)^6}$$

$$R_g^2 = \frac{3}{5}r^2$$

# Scattering from a random coil



Debye form factor

$$g_D(x) = \frac{2}{x^2}\left(x - 1 + e^{-x}\right)$$

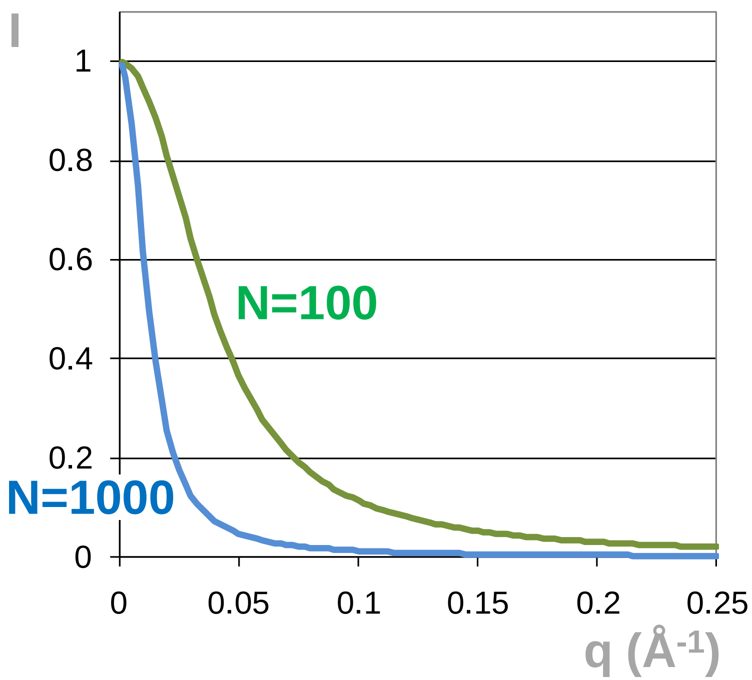
$$x \equiv q^2 R_g^2$$

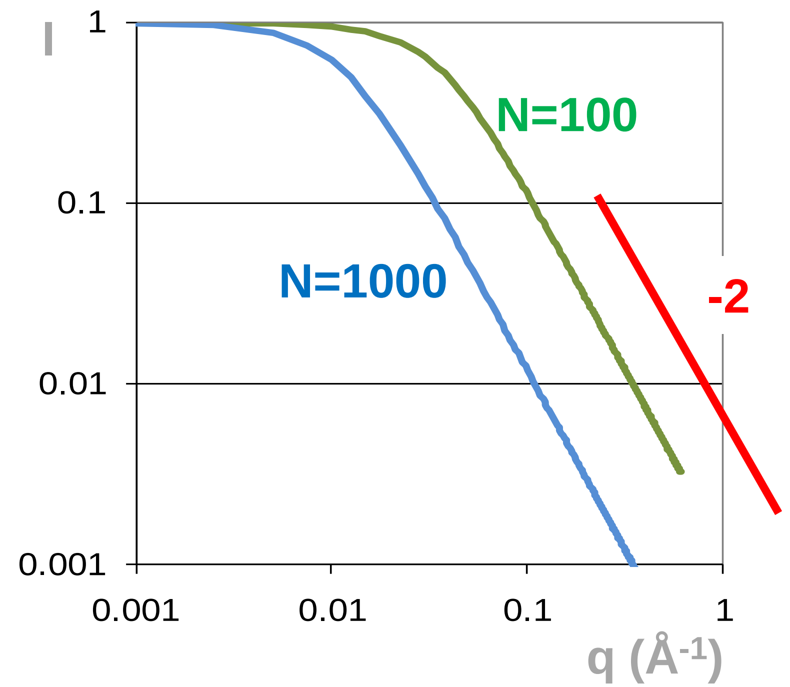
$$R_g^2 = \frac{Na^2}{6}$$

a=10 Å

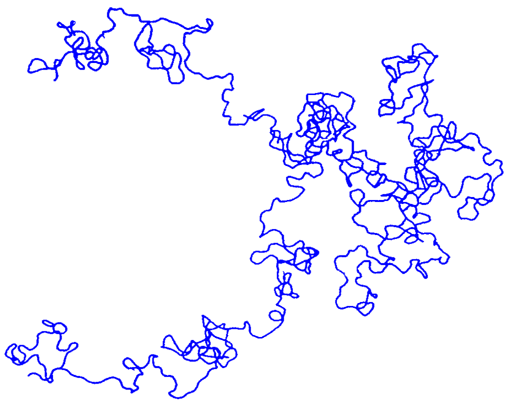
N=100 → Rg≈4nm

N=1000 → Rg≈13nm



# Scattering from a random coil



Debye form factor

$$g_D(x) = \frac{2}{x^2}\left(x - 1 + e^{-x}\right)$$

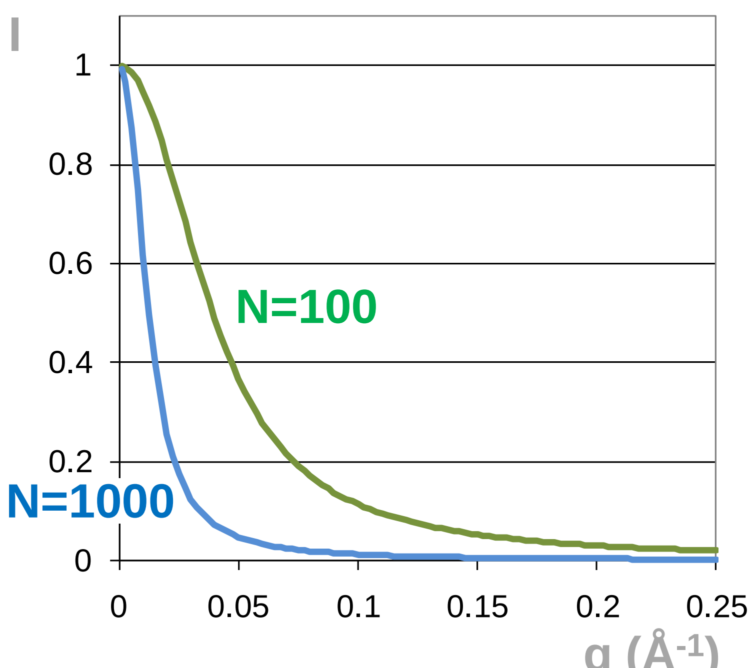
$$x \equiv q^2 R_g^2$$

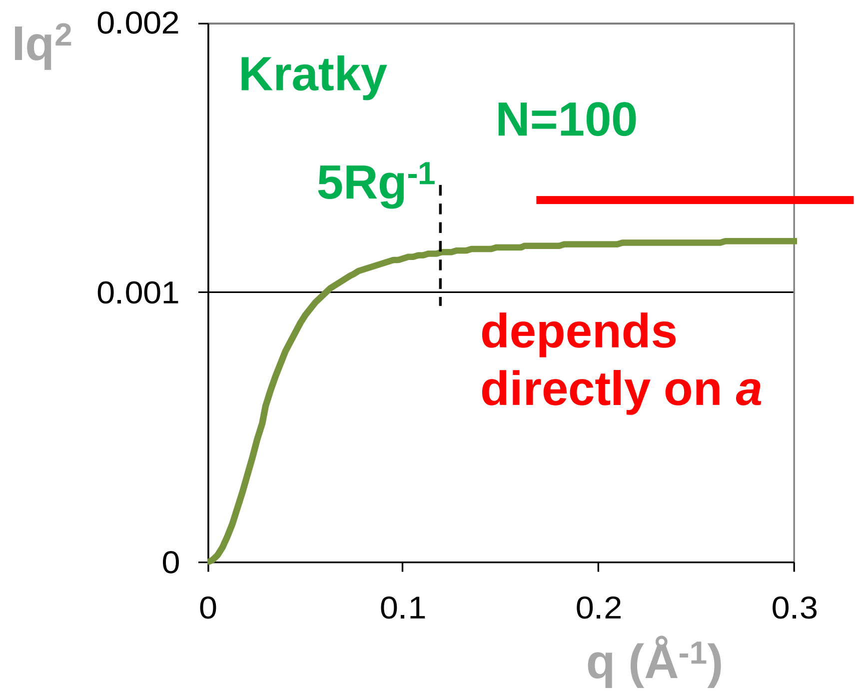
$$R_g^2 = \frac{N a^2}{6}$$

a=10 Å

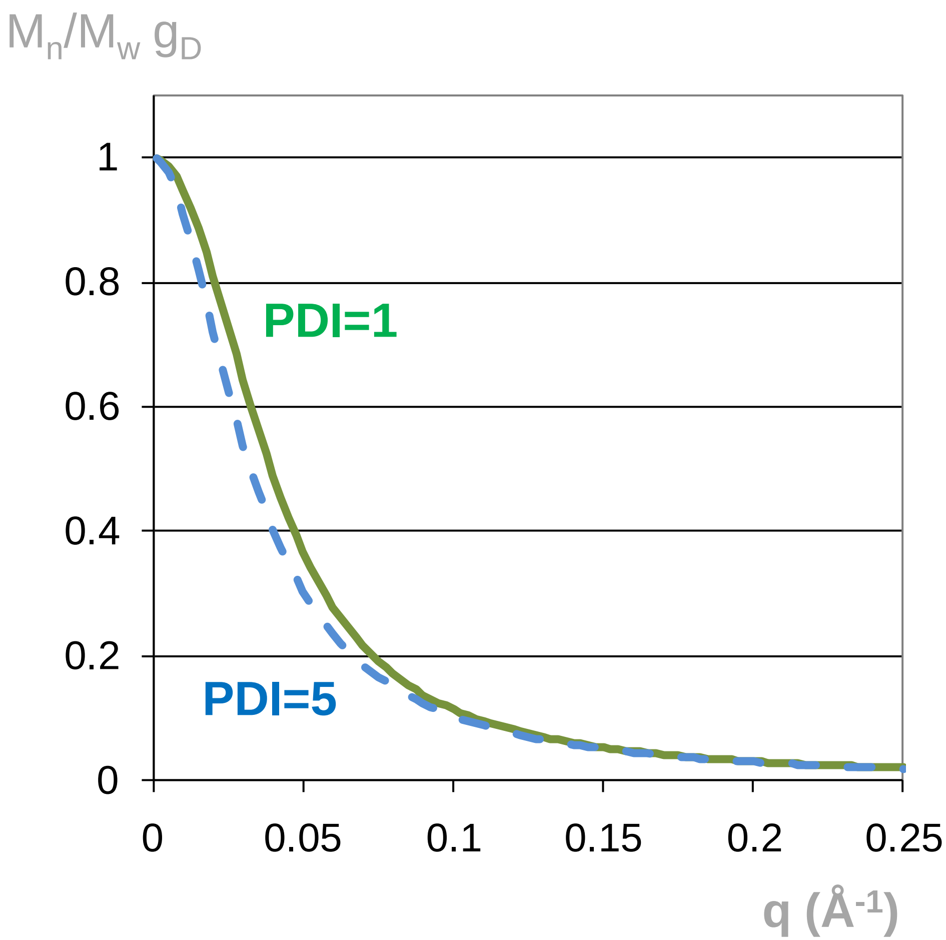
N=100 → Rg≈4nm

N=1000 → Rg≈13nm



# Polydisperse random coils




Polydisperse debye form factor

$$g_D(x) = \frac{2}{(1+1/h)x^2}\left[\left(1+\frac{x}{h}\right)^{-h} - 1 + x\right]$$

$$x \equiv q^2\langle R_g^2\rangle_n \equiv \frac{q^2\langle R_g^2\rangle_z}{1+2/h}$$

$$h = \left(\frac{M_w}{M_n} - 1\right)^{-1}$$

*(normalised to PDI)*

**a=10 Å**

**N=100 → Rg≈4nm**

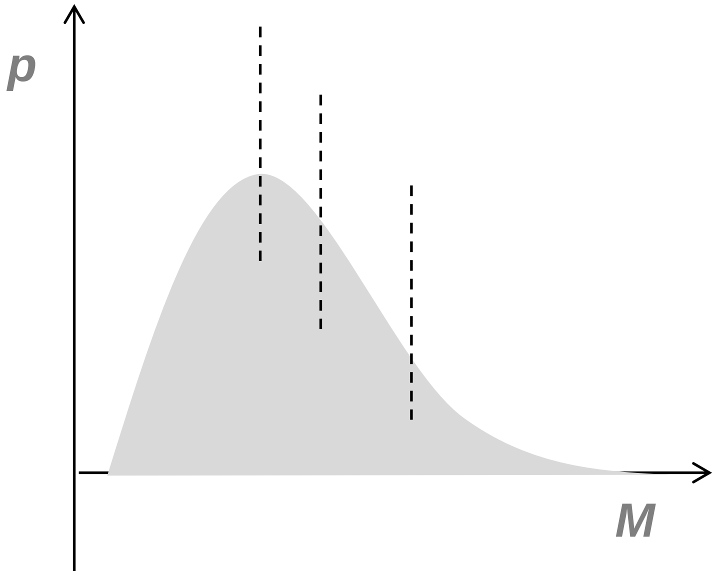
**$N_w$=100, $N_w/N_n$=5**

# A polydispersity model

(Schultz-Zimm)

$$p(M) = \frac{h^h}{\Gamma(h)} \left(\frac{M}{M_n}\right)^h e^{-h\left(\frac{M}{M_n}\right)}$$

$$h = \left(\frac{M_w}{M_n} - 1\right)^{-1}$$

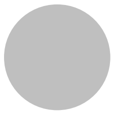


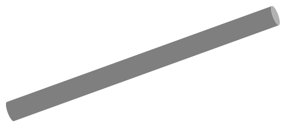
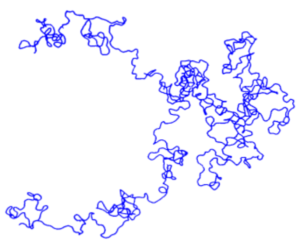
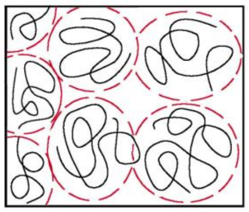

Number average $\quad M_n = \int p(M) M \, dM$

Weight average $\quad M_w = \frac{\int p(M) M^2 dM}{\int p(M) M \, dM} \equiv \frac{\langle M \rangle_2}{\langle M \rangle_1}$

$\mathrm{z-average} \quad M_z = \frac{\int p(M) M^3 dM}{\int p(M) M^2 dM} \equiv \frac{\langle M \rangle_3}{\langle M \rangle_2}$

# Useful form factors



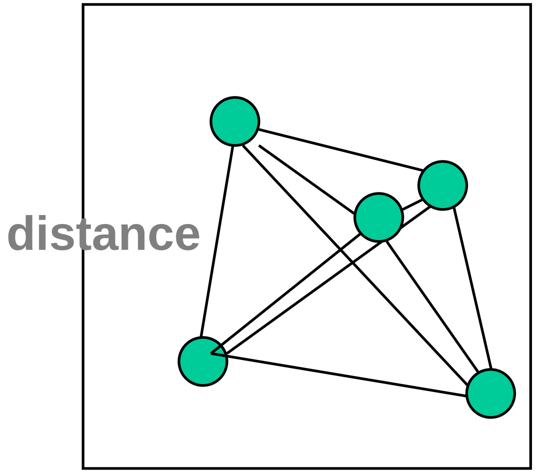




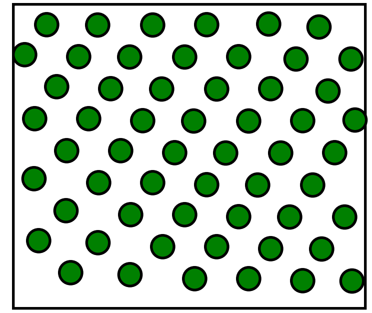
| | |
|---|---|
| Sphere of radius $R_p$ | $P(Q)=\left[\frac{3\,(Sin\,(QR_p)-QR_p\,Cos\,(QR_p))}{(QR_p)^3}\right]^2$ |
| Disc of negligible thickness and radius $R_p$ <br> ($J_1$ is a first-order Bessel function) | $P(Q)=\frac{2}{(QR_p)^2}\left[1-\frac{J_1(2QR_p)}{QR_p}\right]$ |
| Rod of negligible cross-section and length $L$ <br> ($S_i$ is the Sine integral function) | $P(Q)=\frac{2S_i(QL)}{QL}-\frac{Sin^2\,(QL/2)}{(QL/2)}$ |
| Gaussian random coil with z-average radius of gyration $R_g$, polydispersity $(Y+1)$ and <br> $U=\frac{(QR_g)^2}{(1+2Y)}$ | $P(Q)=\frac{2\left[(1+UY)^{-1/Y}+U-1\right]}{(1+Y)\,U^2}$ |
| Concentrated polymer solution with screening length x where <br> $\xi=R_g\left(\frac{\phi}{\phi^*}\right)^{\frac{\nu}{(1-3\nu)}}$ | $P(Q)=P(0)\left[\frac{1}{1+(Q\xi)^2}\right]$ |

S King

http://www.ncnr.nist.gov/resources/

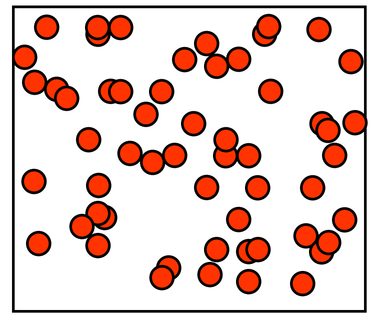
# Structure factor: S



Ordered structure

'crystal'

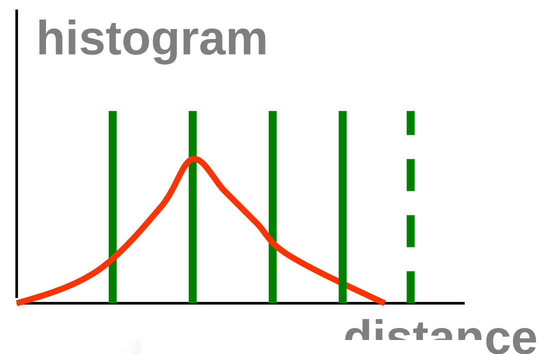


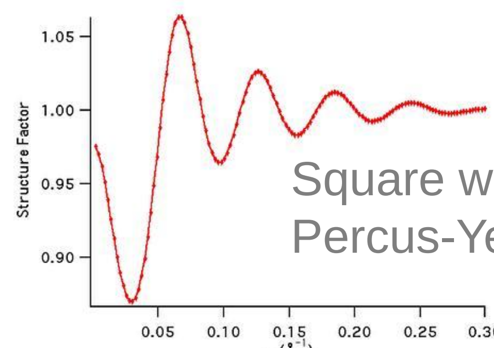
Disordered structure

Interference between radiation scattered by distinct objects

$$S(Q) = 1 + \frac{4\pi N_p}{QV} \int_0^{\infty} [g(r) - 1]\, r \,\mathrm{Sin}\,(Qr)\, dr$$

$$G(r) = \frac{4\pi N_p r^2}{V} g(r)$$



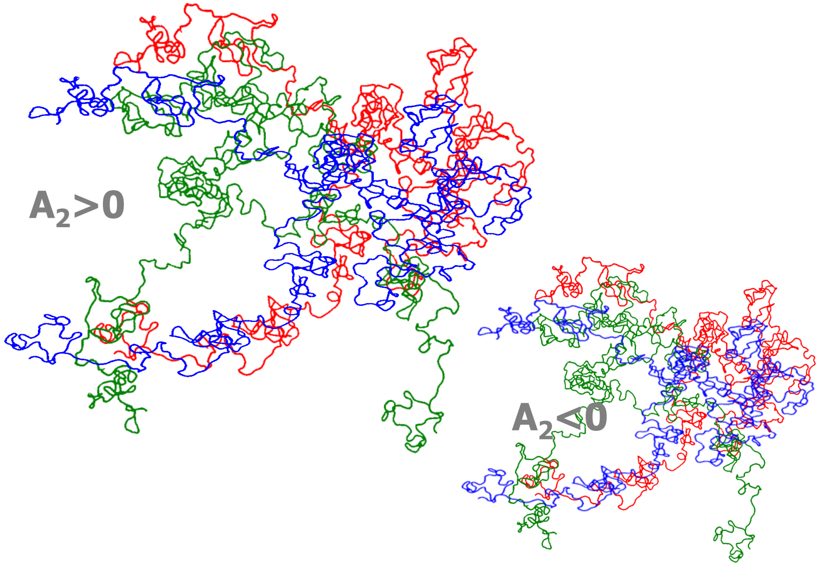



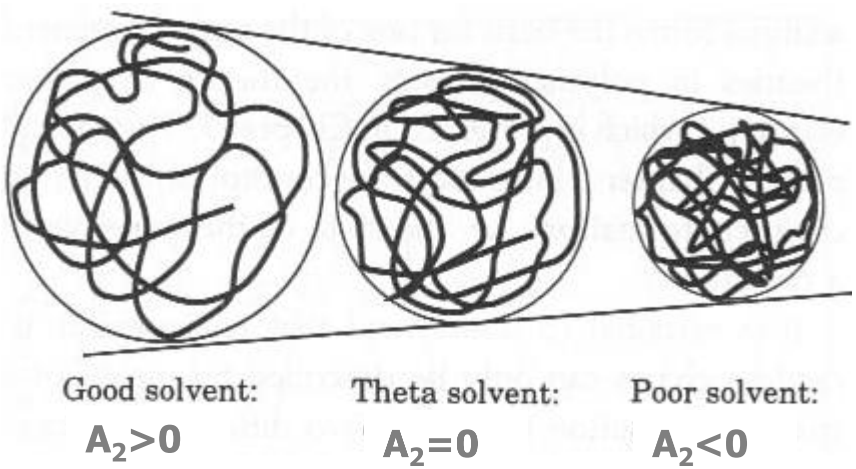

Square well, Percus-Yevick...

Radial distribution function, provides information about their relative position

# Interactions: Polymers in solution and melt

**<u>1953</u> Flory described the shape and size of individual polymer molecules in solutions and melts.**



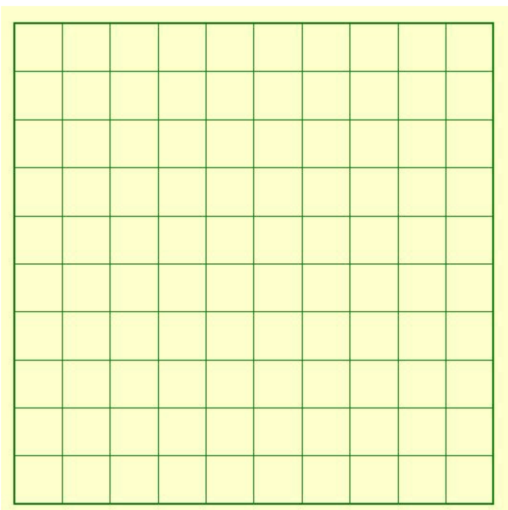




**Ideal chains occur in $\theta$-solutions (ie, neutral solvent, $A_2=0$) or in melt. Chains expand or contract depending on interactions: $A_2$ (Second Virial coeff, for solutions) or $\chi$ (for polymer mixtures)**

# Polymer miscibility (1)

Thermodynamics $\Delta G_m = \Delta H_m - T\Delta S_m$

***Flory-Huggins***
**lattice**



**Binary mixture**

Combinatorial entropy

$$-\frac{\Delta S}{R} = n_A \ln \phi_A + n_B \ln \phi_B$$

$\Omega$ Boltzmann law

Enthalpy $\Delta H_m = K_B T \phi_A \phi_B \chi_{AB}$

$$\frac{\Delta G_m}{K_B T} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \phi_A \phi_B \chi_{AB}$$

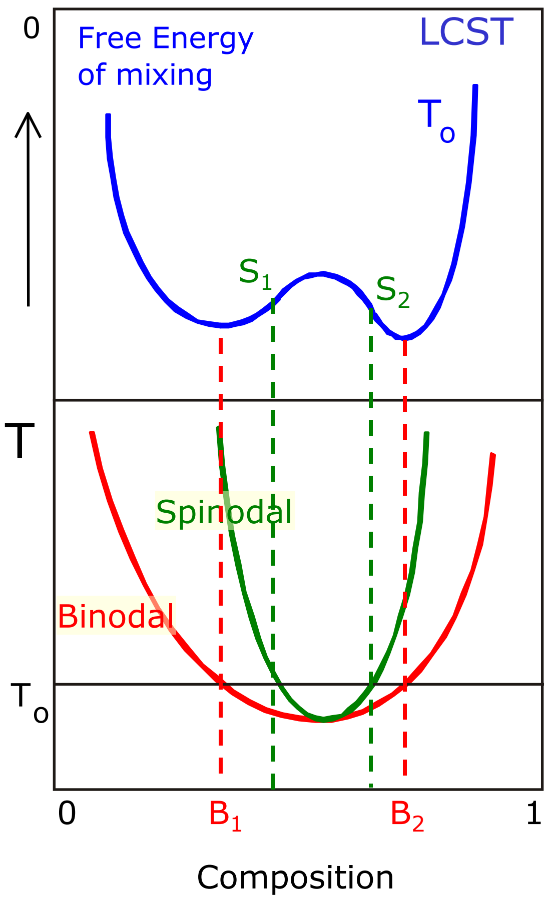
Combinatorial entropy

Enthalpy

$\chi < 0$ mixing occurs $\forall T, \phi$

$\chi > 0$ $\Delta G_m = \Delta H_m - T\Delta S_m$ only at high T

# Polymer miscibility (2)




Thermodynamics $\Delta G_m = \Delta H_m - T\Delta S_m$

$$\frac{\Delta G_m}{k_B T} = \frac{\phi}{v_A N_A}\ln\phi + \frac{(1-\phi)}{v_B N_B}\ln(1-\phi) + \frac{\phi(1-\phi)}{v}\chi$$

Combinatorial entropy

Enthalpy

Phase boundaries?

Binodal

$$\begin{cases} \dfrac{\partial \Delta G_m}{\partial \phi_{B1}} = \dfrac{\partial \Delta G_m}{\partial \phi_{B2}} \equiv \mu \\ \Delta G_m(\phi_{B1}) + \Delta G_m(\phi_{B2}) = \min \end{cases}$$

'minima'

Spinodal

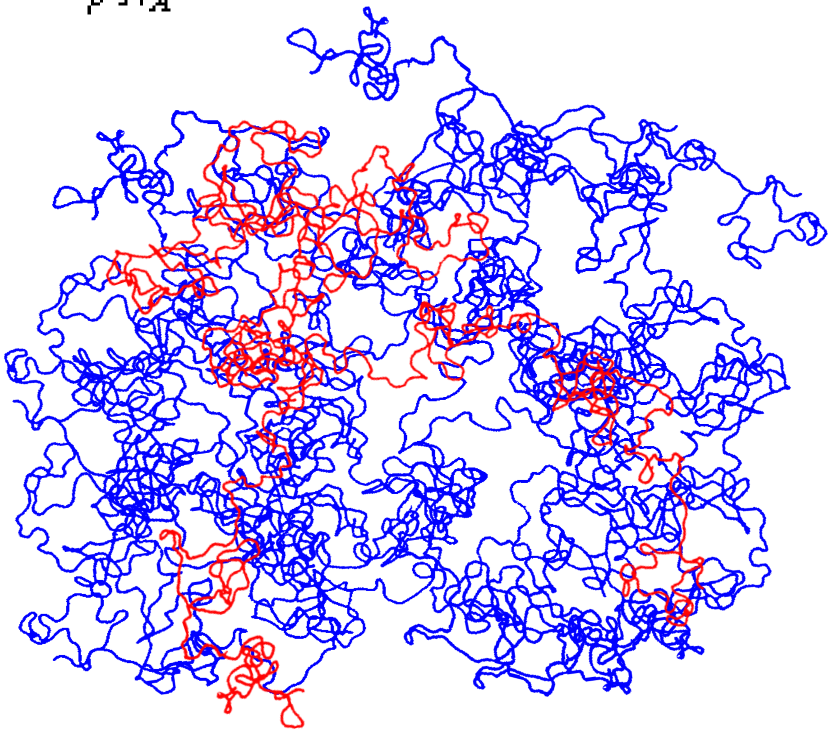
$$\frac{\partial^2 \Delta G_m}{\partial \phi^2} = 0$$

inflection points

# Isotopic polymer mixture

$$\frac{\partial\sigma}{\partial\Omega}(q) = (b_D - b_H)^2 S_{DD}(q) = (b_D - b_H)^2\,\phi(1-\phi) N z^2 P(q)$$

$$\begin{aligned}\frac{1}{V}\,\frac{d\sigma}{d\Omega}(q)\bigg|_{cm^{-1}} &= (b_D - b_H)^2\,\phi(1-\phi)\,\langle M\rangle_w\,\frac{\rho\,N_A}{m^2}\,P(q)\\ &= (b_D - b_H)^2\,\phi(1-\phi)\,\langle M\rangle_w\,\frac{(\Delta\varrho)^2}{\rho\,N_A}\,P(q)\end{aligned}$$



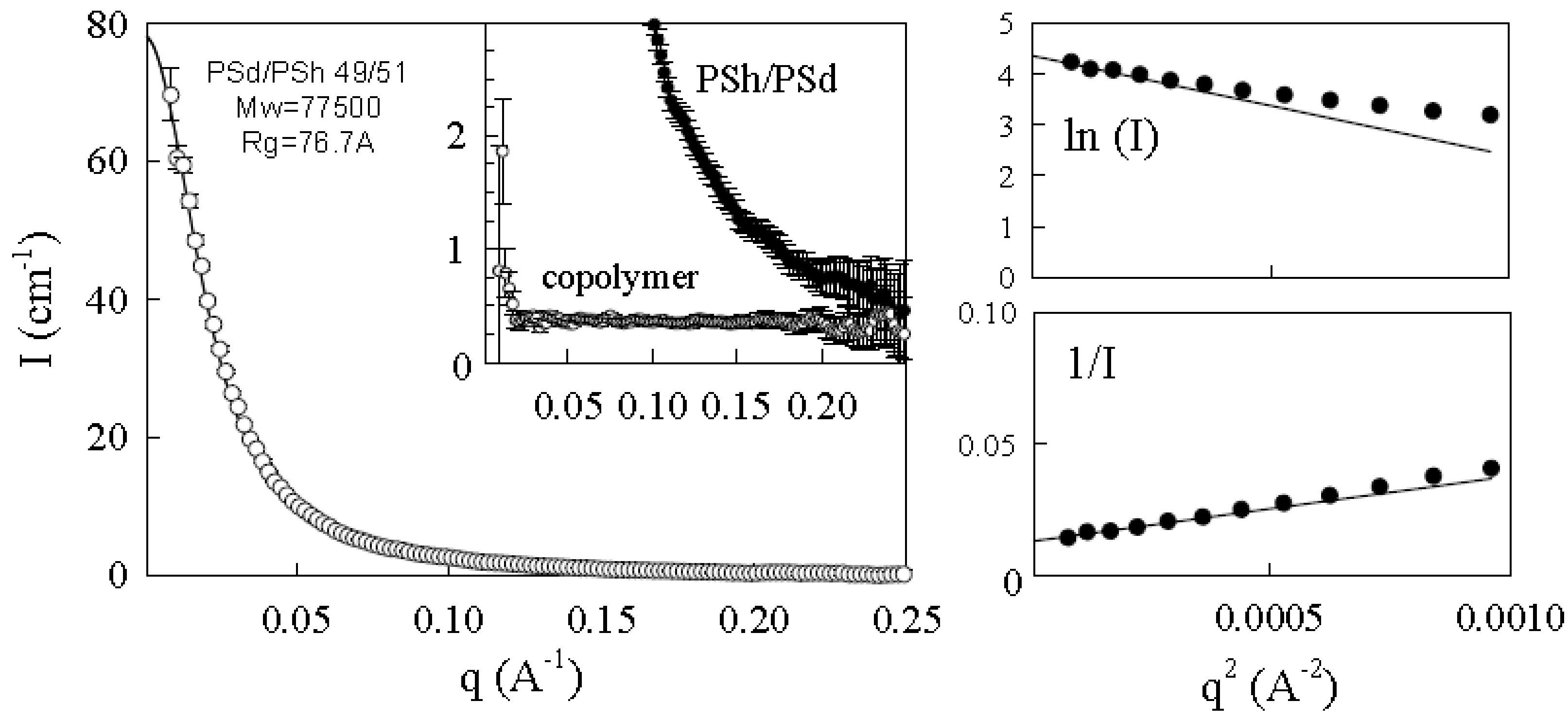
# Approximations: Guinier & Zimm

$$\text{Guinier :}\quad \frac{d\Sigma(q)}{d\Omega} \approx \frac{d\Sigma(0)}{d\Omega}\left(-\frac{(qR_g)^2}{3}\right)$$

$$\text{Zimm :}\quad \left[\frac{d\Sigma(q)}{d\Omega}\right]^{-1} \approx \left[\frac{d\Sigma(0)}{d\Omega}\right]^{-1}\left[1+\frac{(qR_g)^2}{3}\right]$$

where $$\frac{d\Sigma(0)}{d\Omega} = \frac{\phi(1-\phi)\ M_w\ (\Delta\varrho)^2}{N_A\ \rho}$$

for a polymer coil



# Interacting polymer mixtures

$$\frac{1}{V}\frac{d\sigma}{d\Omega}(q)\Big|_{cm^{-1}} = N_A\left(\frac{b_1}{v_1}-\frac{b_2}{v_2}\right)^2 S(q)$$

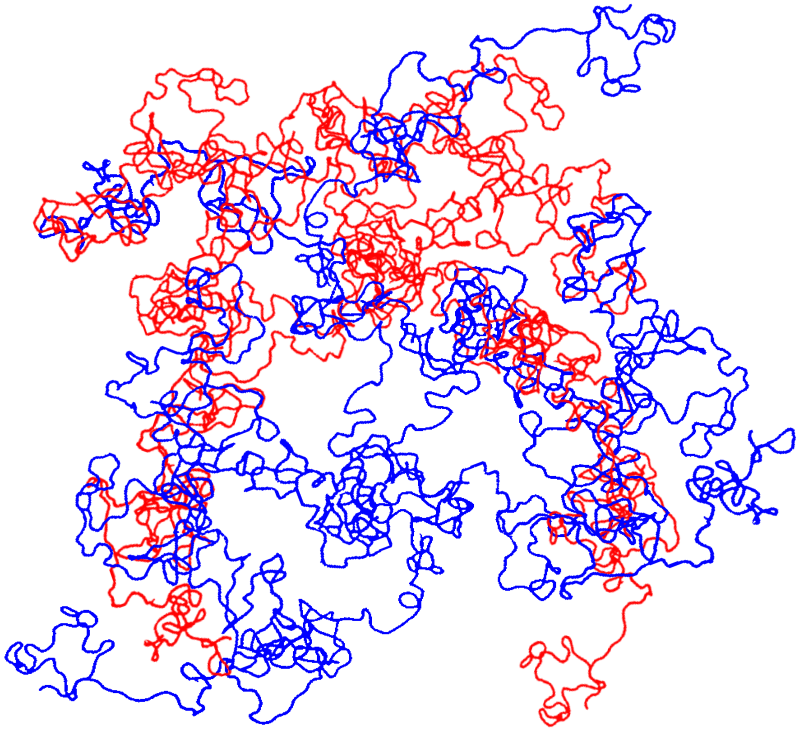
$$\frac{1}{S(q)} = \frac{1}{S_1(q)} + \frac{1}{S_2(q)} - 2\frac{\tilde{\chi}_{12}}{v_0}$$

$$S_i(q) = \phi_i v_i \langle N_i\rangle_n \langle g_D(R_{gi}^2 q^2)\rangle_w$$

**Zimm** $$S_i(q) \approx \phi_i v_i \langle N_i\rangle_w \left(1 - \frac{1}{3}\langle R_{gi}^2\rangle_z q^2\right)$$

$$\frac{1}{S(q)} = \frac{1}{S(0)}\left[1 + \frac{1}{3}R_{app}^2 q^2\right]$$ where $$R_{app}^2 = \left(\frac{\langle R_{g1}^2\rangle_z}{\phi_1 v_1 \langle N_1\rangle_w} + \frac{\langle R_{g2}^2\rangle_z}{\phi_2 v_2 \langle N_2\rangle_w}\right) S(0)$$

$$\frac{1}{S(0)} = \frac{1}{\phi_1 v_1 \langle N_1\rangle_w} + \frac{1}{\phi_2 v_2 \langle N_2\rangle_w} - 2\frac{\tilde{\chi}_{12}}{v_0}$$

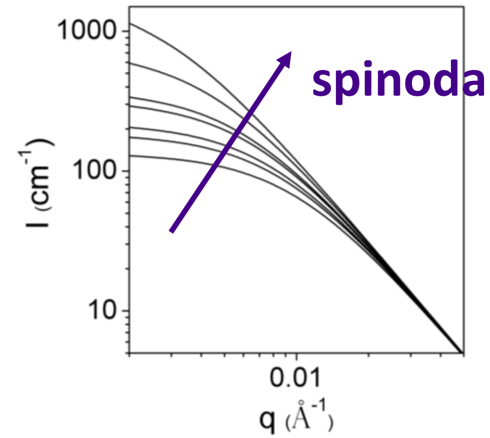


# Random Phase Approximation

**RPA (de Gennes, 1979):**

$$\frac{1}{S(q)} = \frac{1}{S_1(q)} + \frac{1}{S_2(q)} - 2\frac{\tilde{\chi}_{12}}{v_o}$$

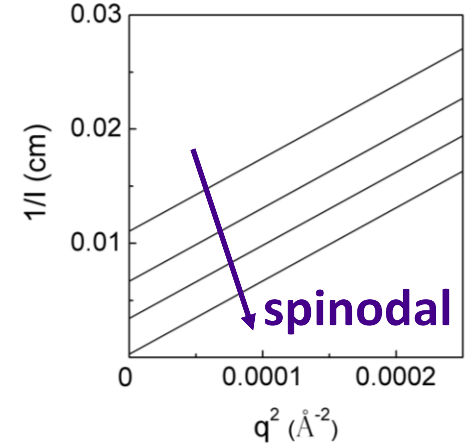
1/S(0) = G''




**Ornstein-Zenike:**

At low angle (qRg << 1),

$$S(q) = \frac{S(0)}{1+\xi^2 q^2}$$

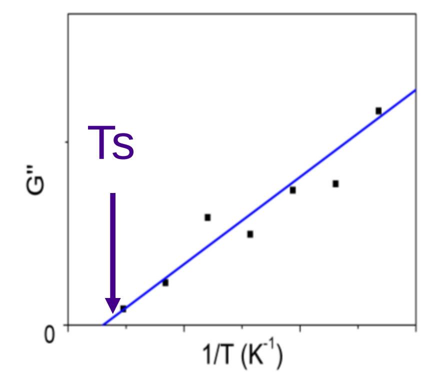



Linear in the Zimm representation as:

$$1/S(q) = 1/S(0) + Aq^2$$

$$\frac{1}{S(q)} = 2(\chi_S - \chi_F) + \frac{\xi^2}{S(0)} q^2$$

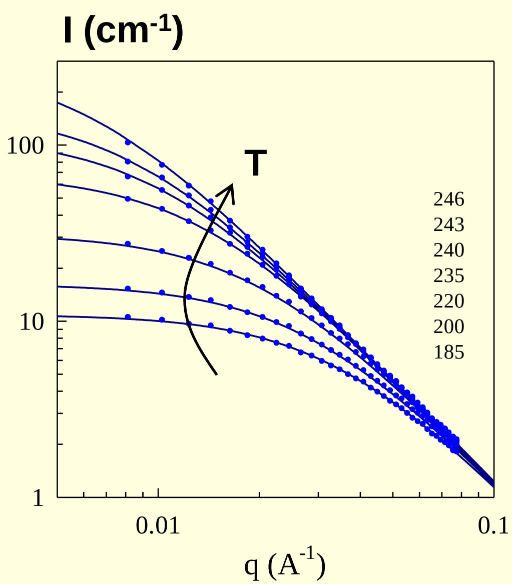
$T_s$ determined by extrapolation of G'' to 0



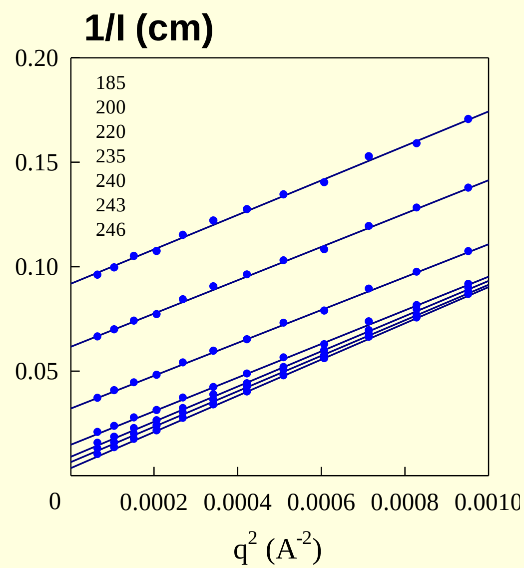
# Equilibrium: SANS

TMPC/PSd 50/50

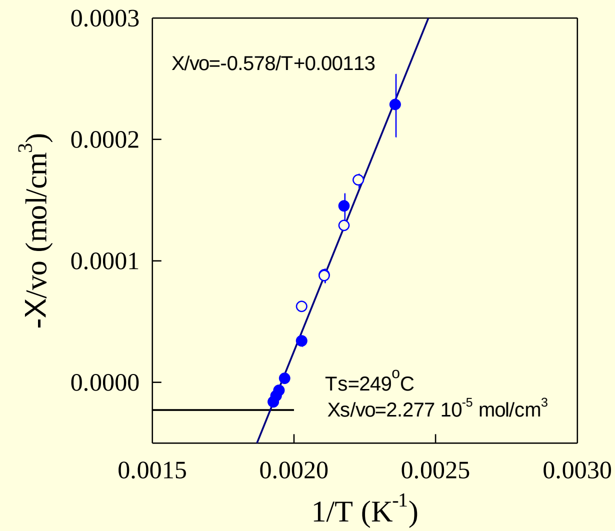
**1-phase scattering**




**Orstein-Zernike**




**Interaction $\chi$FH**



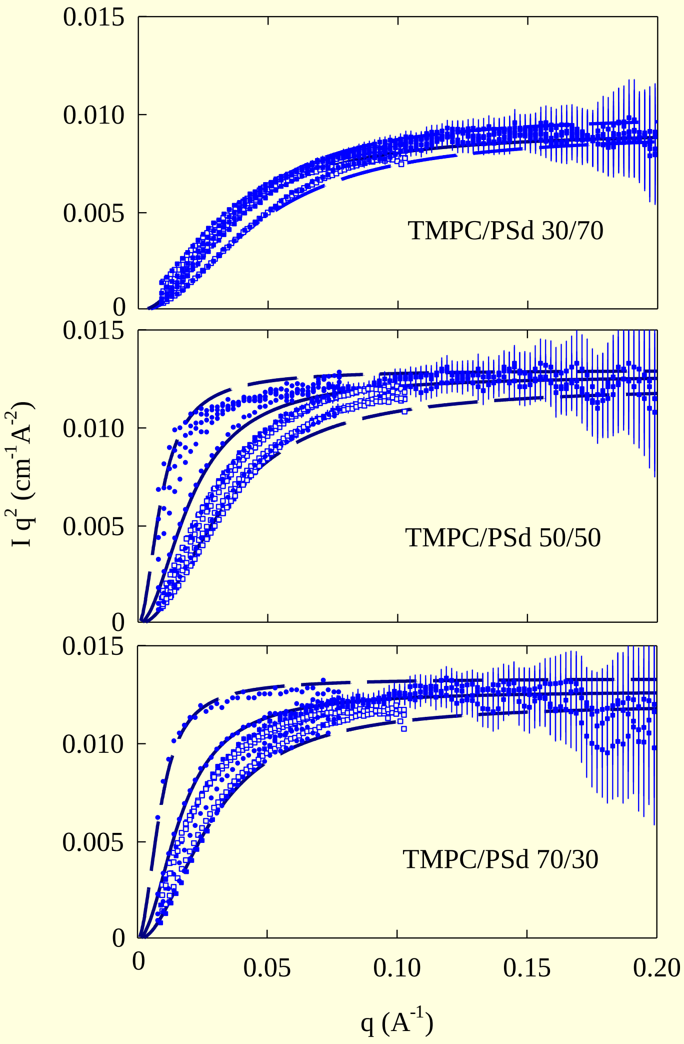

## Random Phase Approximation

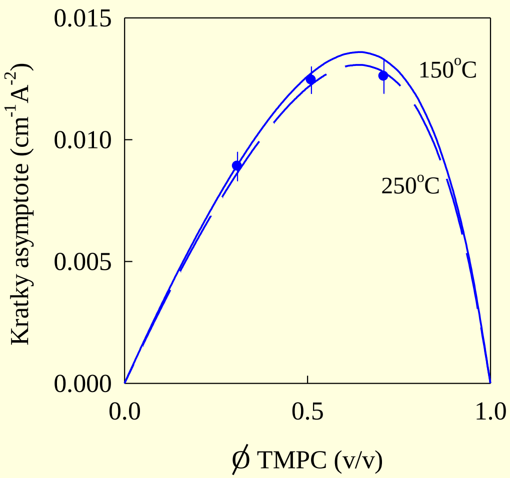
$$\frac{1}{S_{AB}(q)} = \frac{1}{\phi_A v_A \langle N_A \rangle_n \langle g_D(q)_A \rangle_w} + \frac{1}{\phi_B v_B \langle N_B \rangle_n \langle g_D(q)_B \rangle_w} - 2\frac{\tilde{\chi}_{AB}}{v_o}$$

$$\frac{1}{S(q)} = 2(\chi_S - \chi_F) + \frac{\xi^2}{S(0)} q^2$$

$$\xi^2 = \frac{v_0}{36(\tilde{\chi}_S - \tilde{\chi}_{AB})}\left( \frac{\langle N_A \rangle_z}{\langle N_A \rangle_w} \frac{a_A{}^2}{\phi_A v_A} + \frac{\langle N_B \rangle_z}{\langle N_B \rangle_w} \frac{a_B{}^2}{\phi_B v_B} \right)$$

# Equilibrium: Kratky asymptote



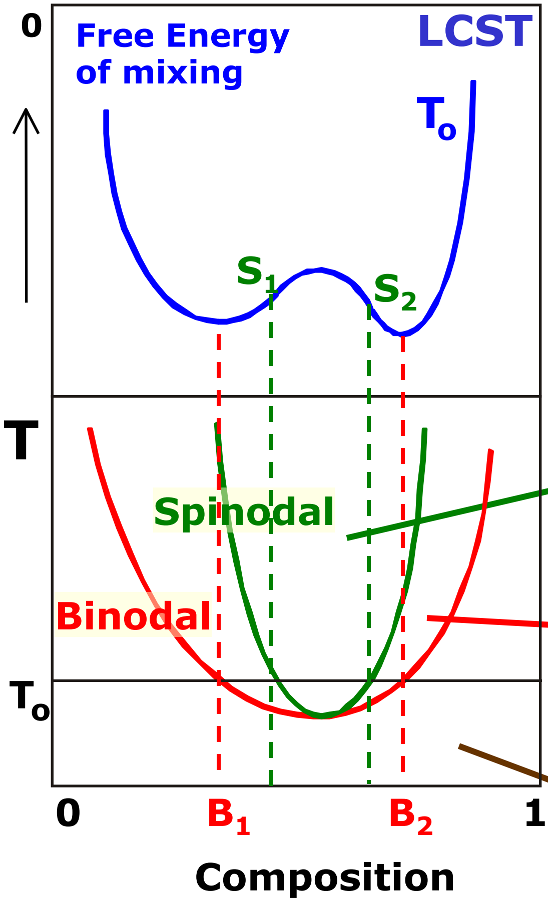




## Kratky asymptote and segment length

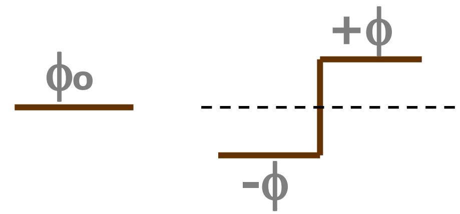
$$S(q) \approx \frac{12\phi_1\phi_2}{q^2}\frac{v_o}{\hat{a}^2}$$

$$\frac{\hat{a}^2}{v_0} \equiv \phi 1 \phi 2\left(\frac{a_1^{\ 2}}{\phi_1 v_1} + \frac{a_2^{\ 2}}{\phi_2 v_2}\right)$$

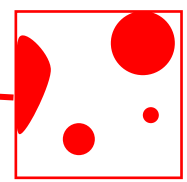
# Non-equilibrium: Fluctuations & Phase separation



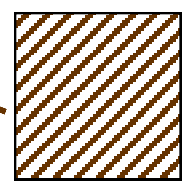

**Concentration fluctuations**




**Unstable:** $G'' < 0$
***spinodal decomposition***

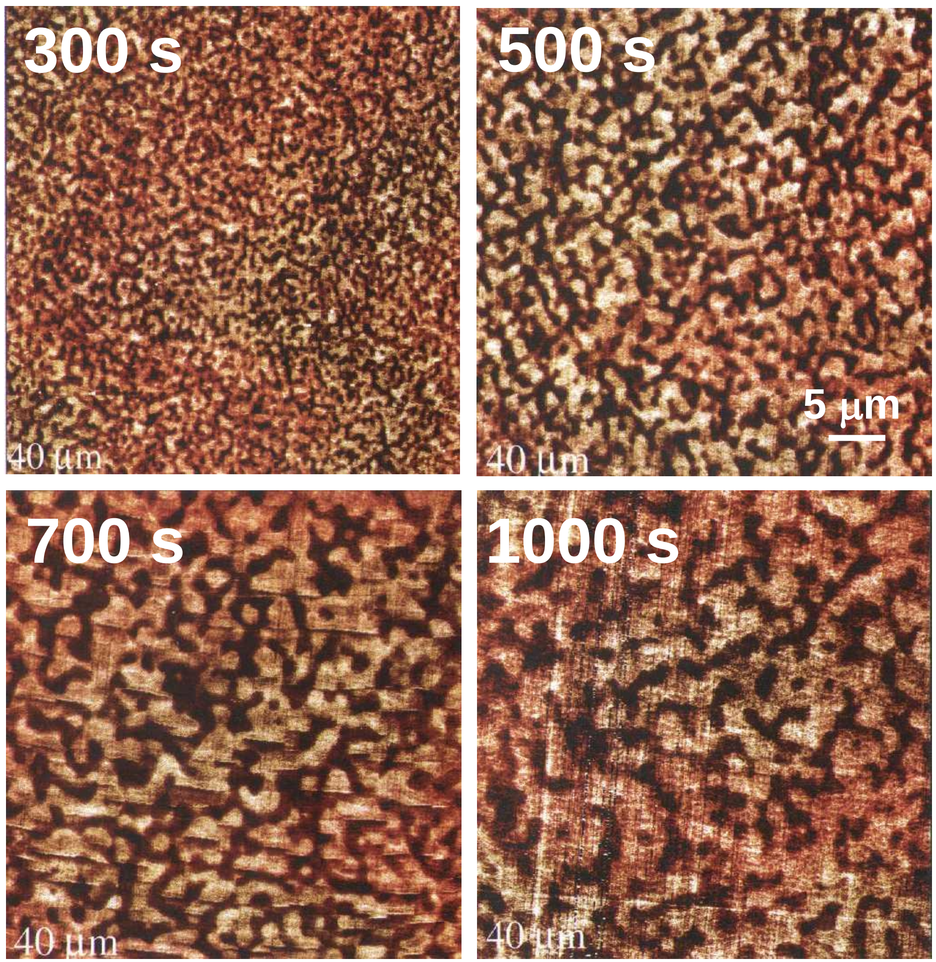


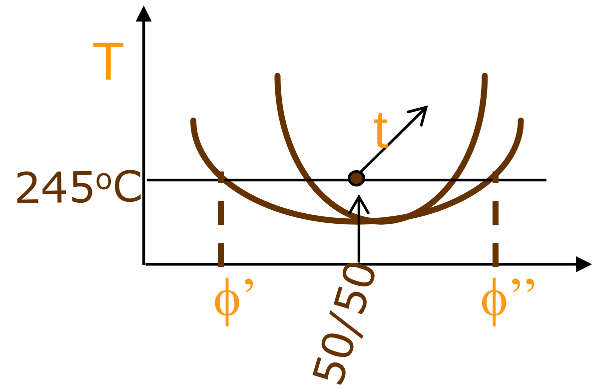
**Metastable:**
***nucleation & growth***

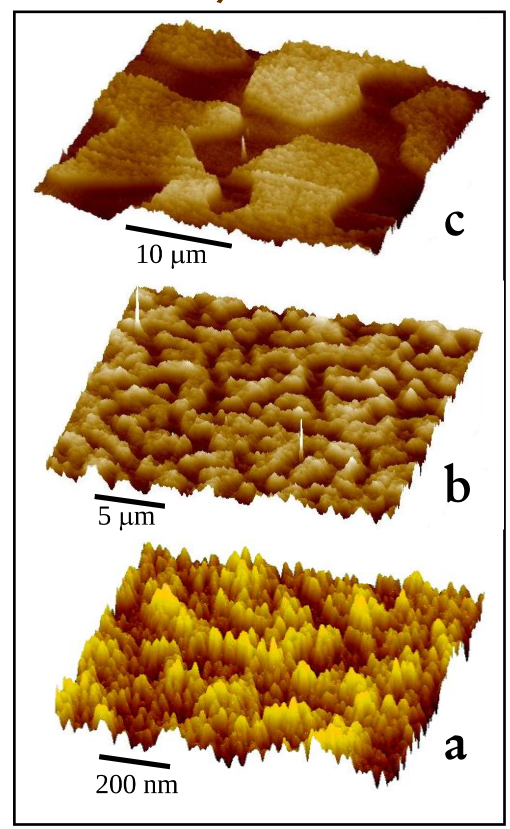


**Stable:**
***equilibrium***

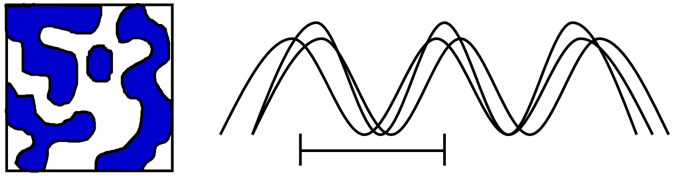
# Phase separation: spinodal decomposition



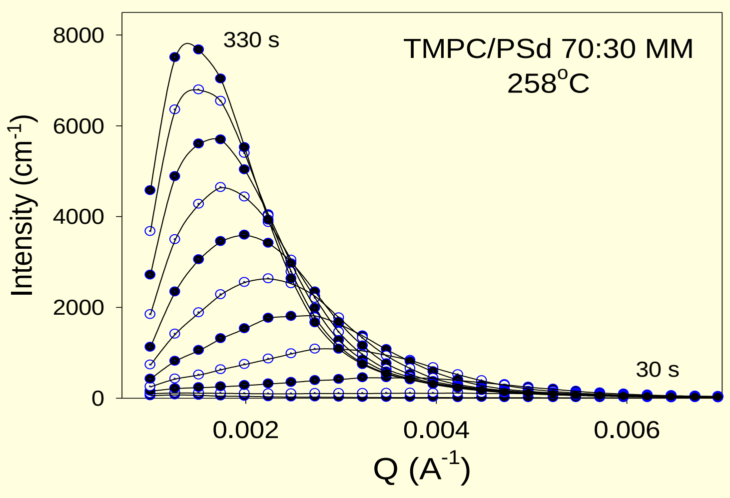



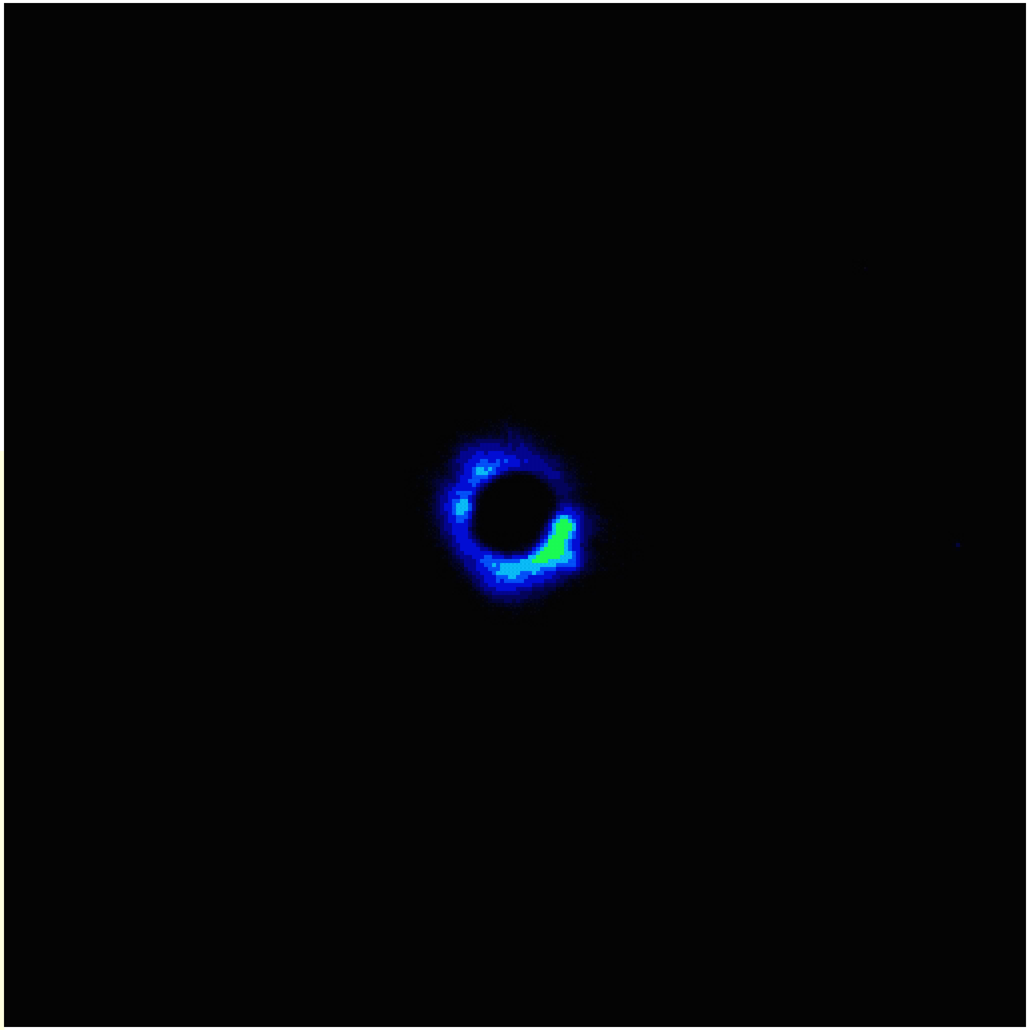



# Phase separation

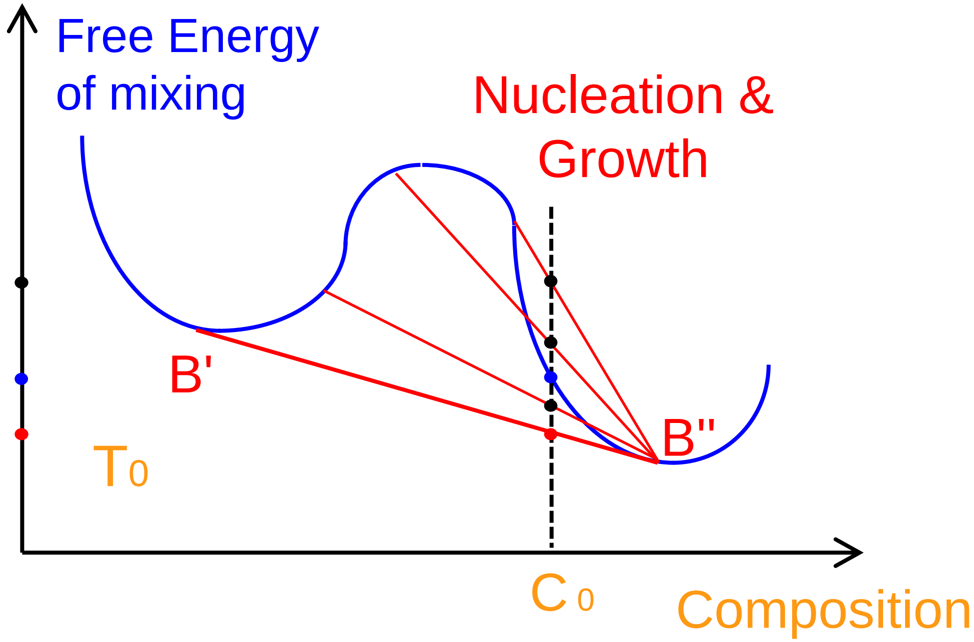


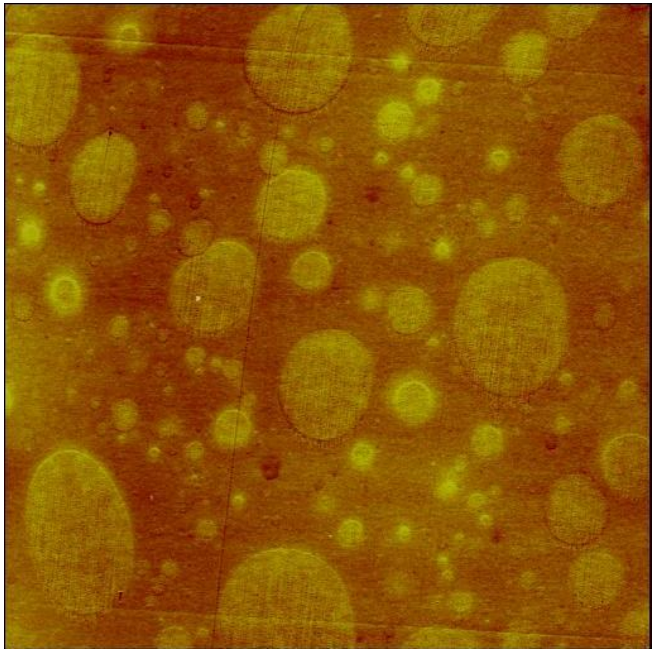
$\Lambda_m$: characteristic length of phase separation ~10s-100s nm



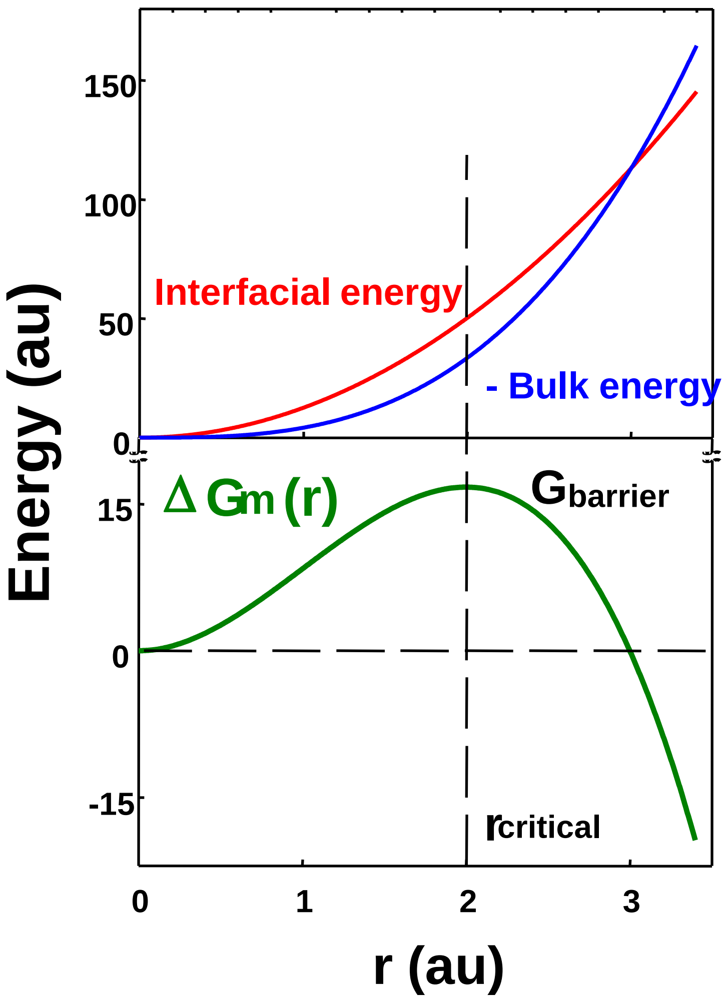
# Nucleation & Growth

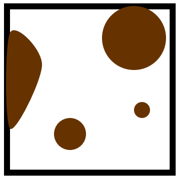


Comparatively SLOW,
since activated process

# Nucleation & Growth



**Energy balance**

$$\Delta G(r) = -\frac{4\pi}{3} r^3 \Delta g + 4\pi r^2 \sigma$$

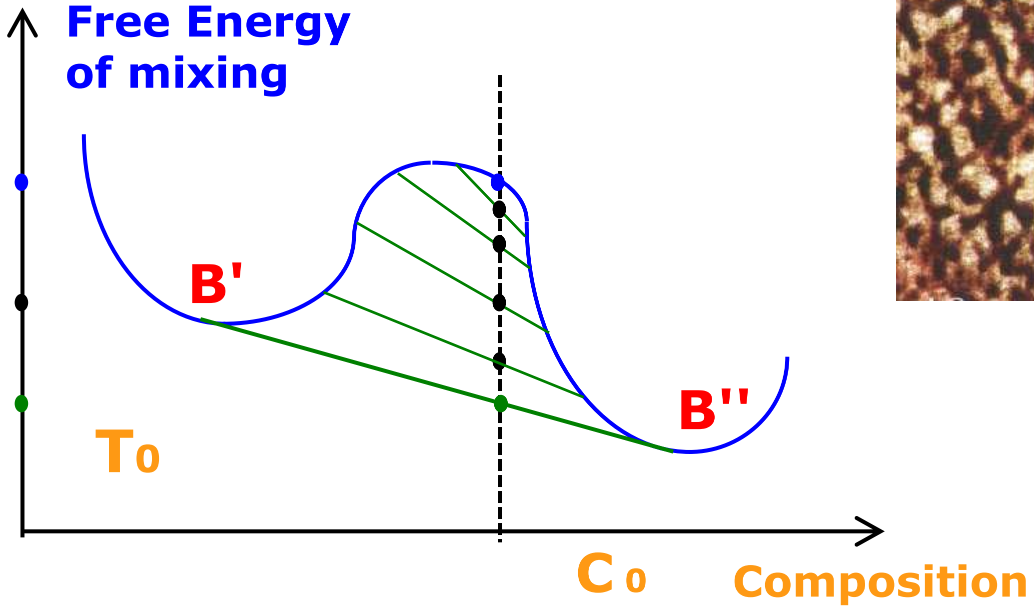
**bulk** **interface**

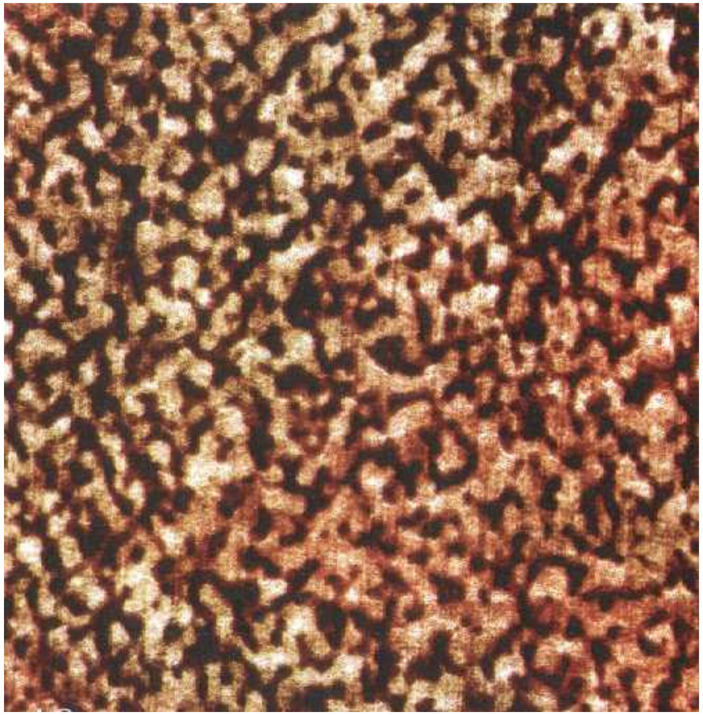
→ **Critical droplet**

$$\Delta G_{barrier} = \frac{16\pi\sigma^3}{3\Delta g^2}$$

$r_c = 2\sigma/\Delta g$

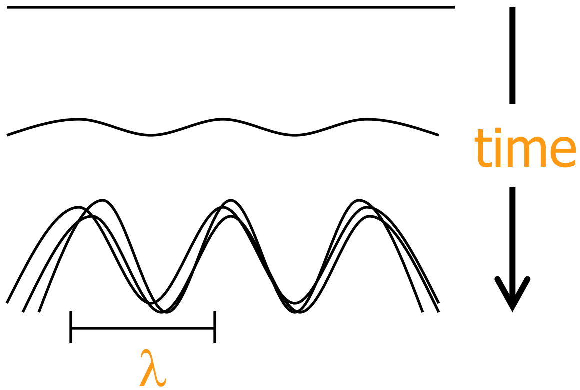
# Spinodal decomposition

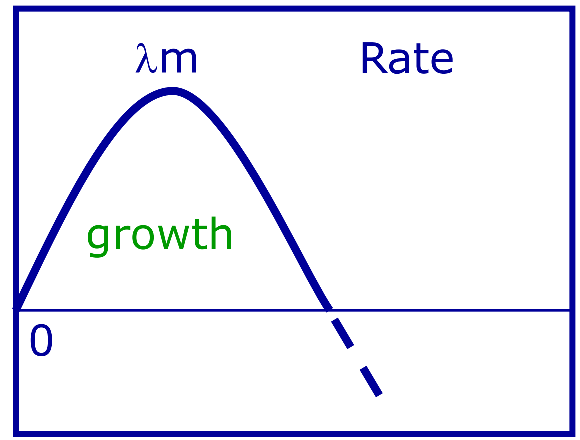


FAST, spontaneous

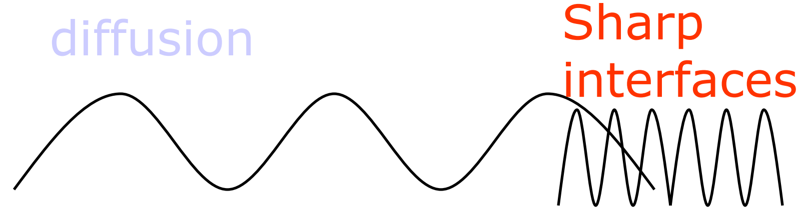
# Spinodal decomposition



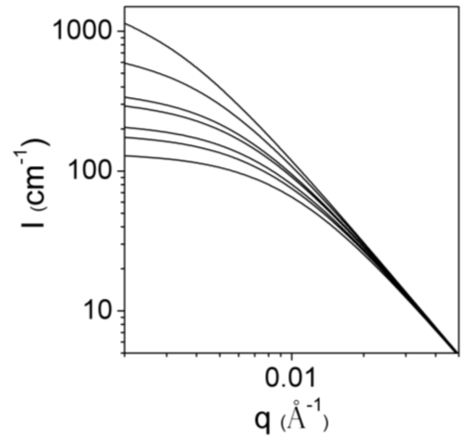

concentration fluctuations

$$\phi = \phi_o + \tilde{\phi}$$




$$Rate\,(\lambda) = -A\frac{\partial^2 G}{\partial \Phi^2}(1/\lambda)^2 - B(1/\lambda)^4$$

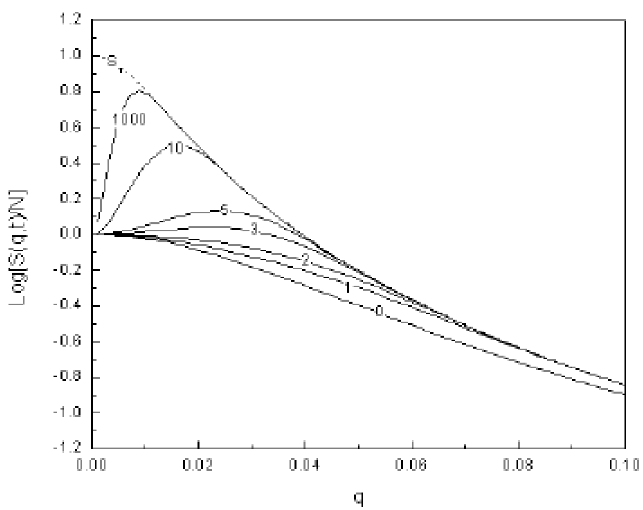
# Cahn-Hilliard Cook theory

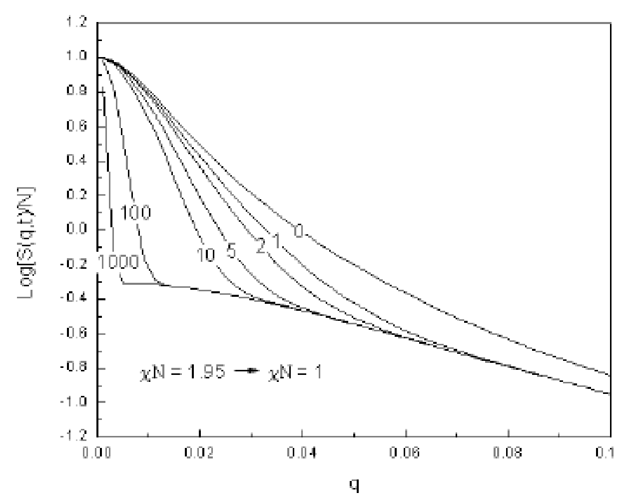



$$S(q,t) = S_T(q) + [S(q,0) - S_T(q)]\exp^{-2\tau_q^{-1}t}$$

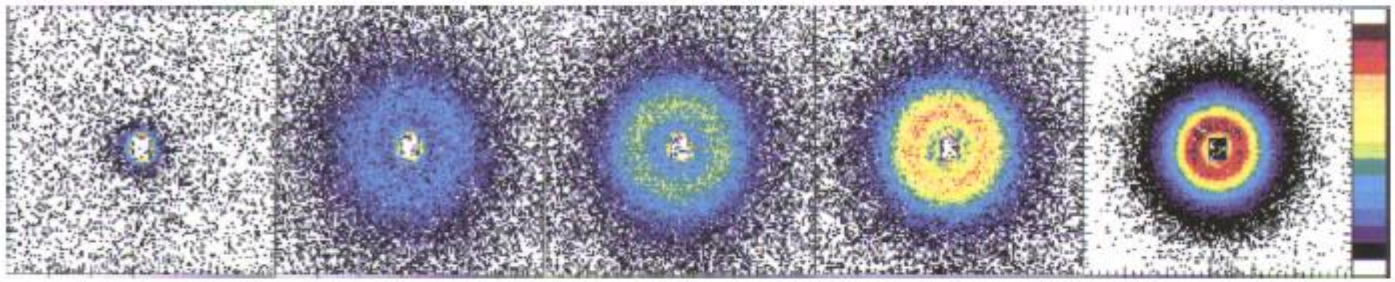
$$\tau_q^{-1} = q^2\Lambda(q)S_T^{-1}(q)$$

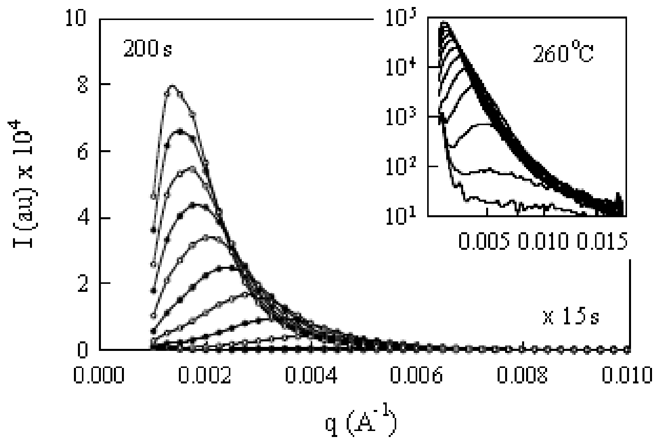
$$\begin{aligned} \Lambda(q) &= Wa^2\phi(1-\phi)g_D(q) && (Rouse\ Model) \\ \Lambda(q) &= \frac{Wd^2}{Z}\phi(1-\phi)g_D(q) && (Reptation\ Model) \end{aligned}$$



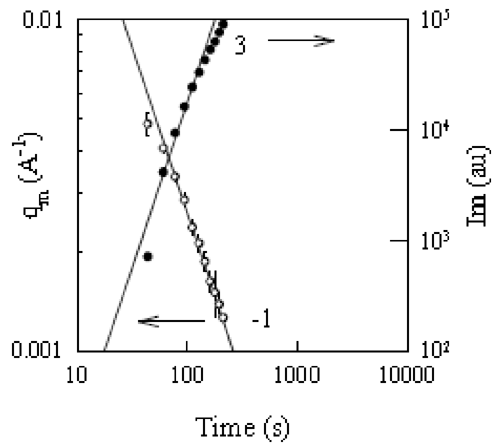




**Spatially resolved “rheology”**

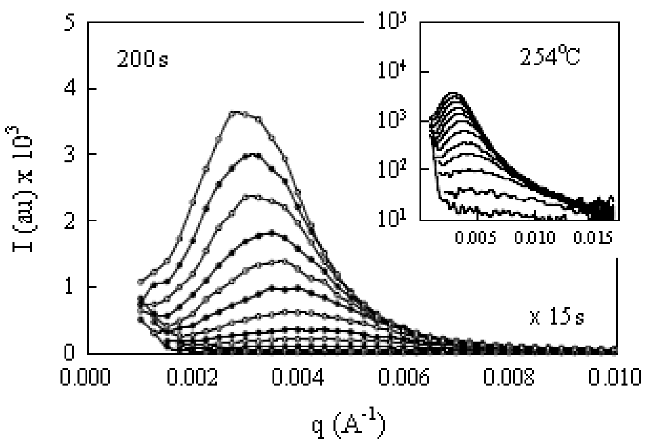




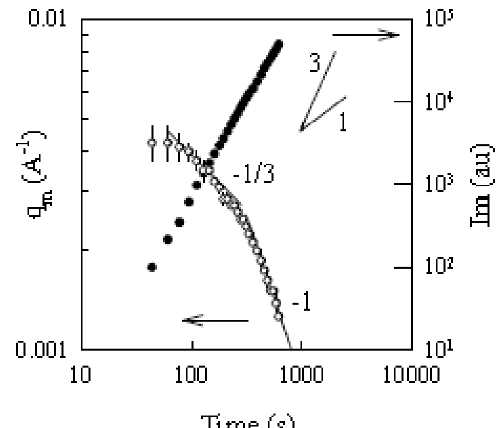
200 s
260°C
x 15 s
I (au) x $10^4$
q ($A^{-1}$)
0.005 0.010 0.015

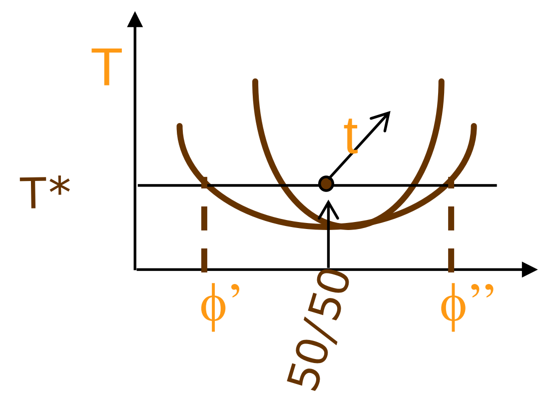
3
-1
$q_m$ ($A^{-1}$)
Im (au)
Time (s)

200 s
254°C
x 15 s
I (au) x $10^3$
q ($A^{-1}$)
0.005 0.010 0.015

3
1
-1/3
-1
$q_m$ ($A^{-1}$)
Im (au)
Time (s)

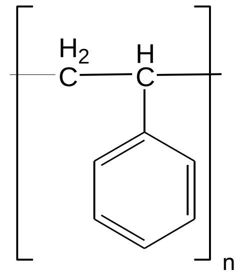



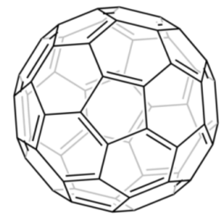
T
t
T*
φ'
50/50
φ''

# Opportunities & recent developments

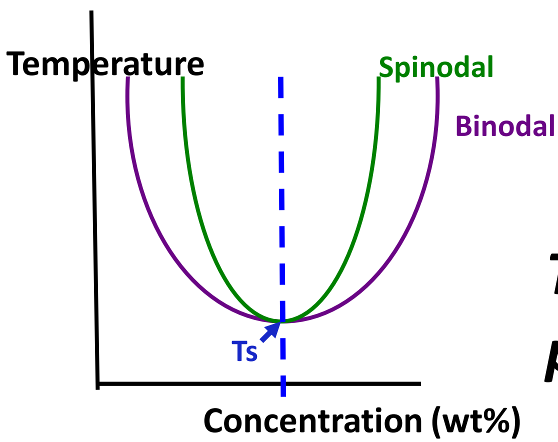
**nano***composites*

**structure**



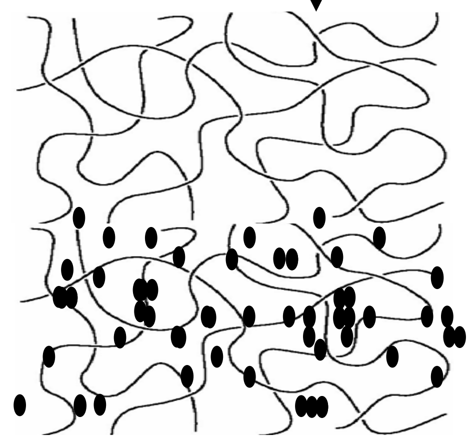



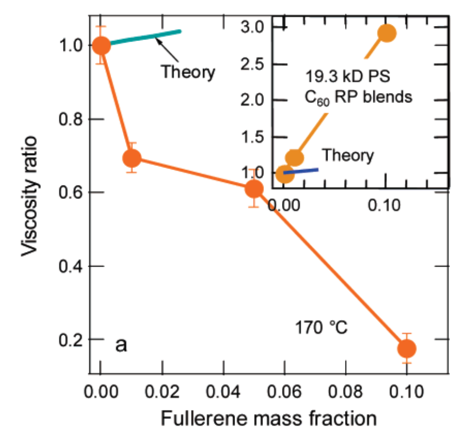
**dynamics**




**Bulk**

***Thermodynamics & phase separation***

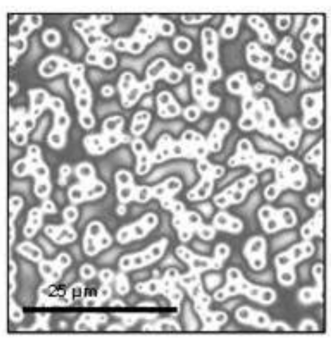





Tuteja et al. Nat. Mat. (2003) 2, 762

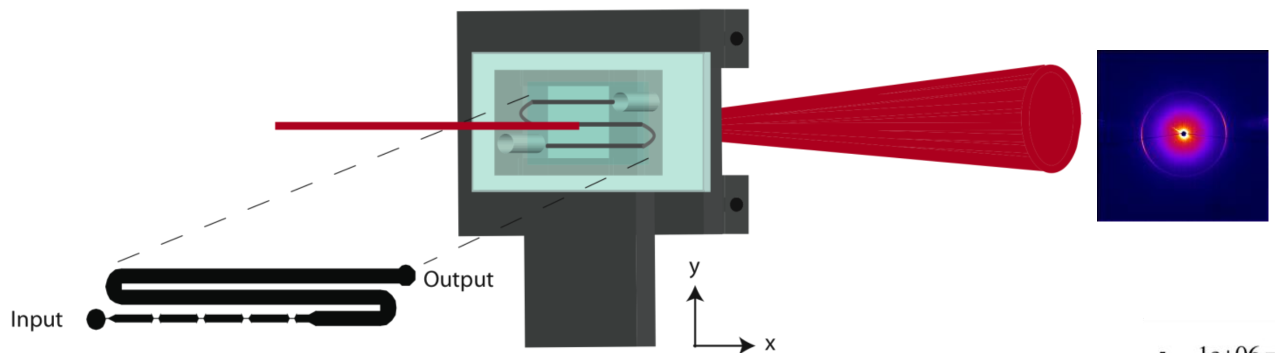
**Thin Films**

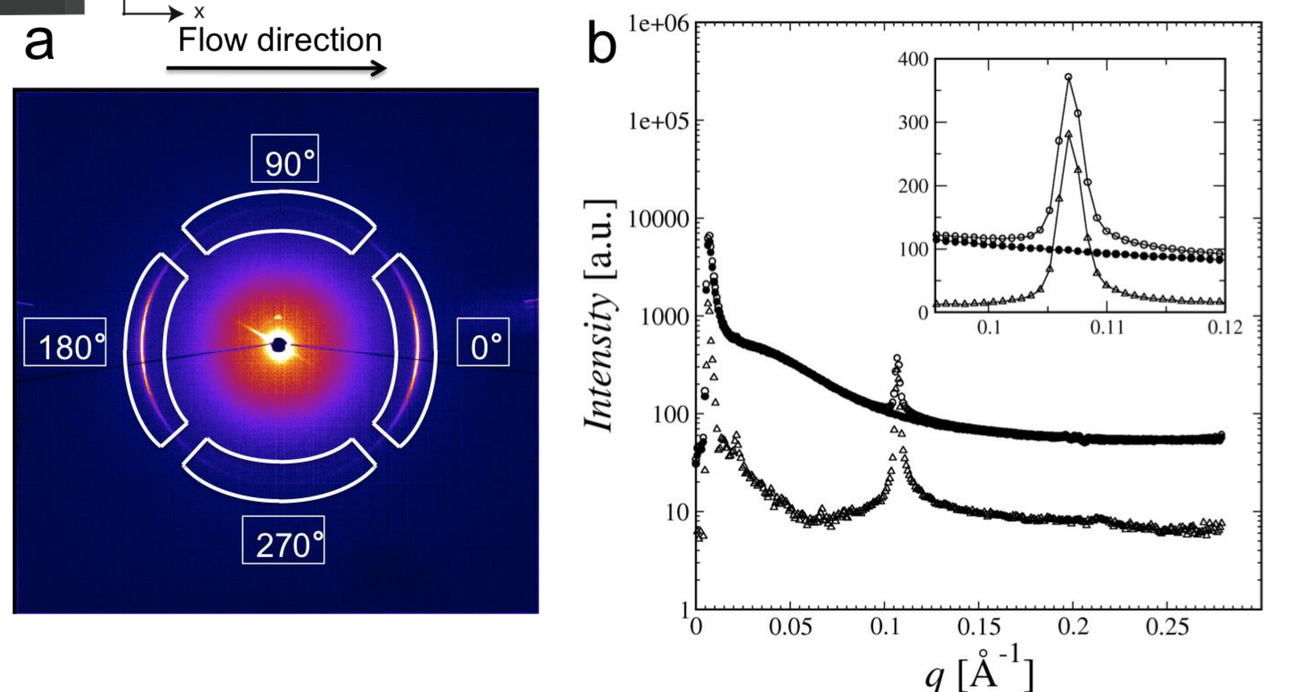
***Morphology***



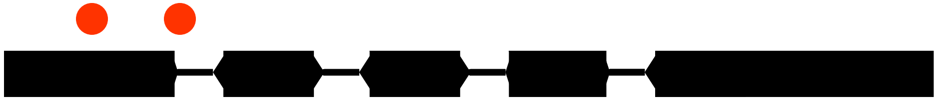
# **Flow fields** (and microfluidics?)

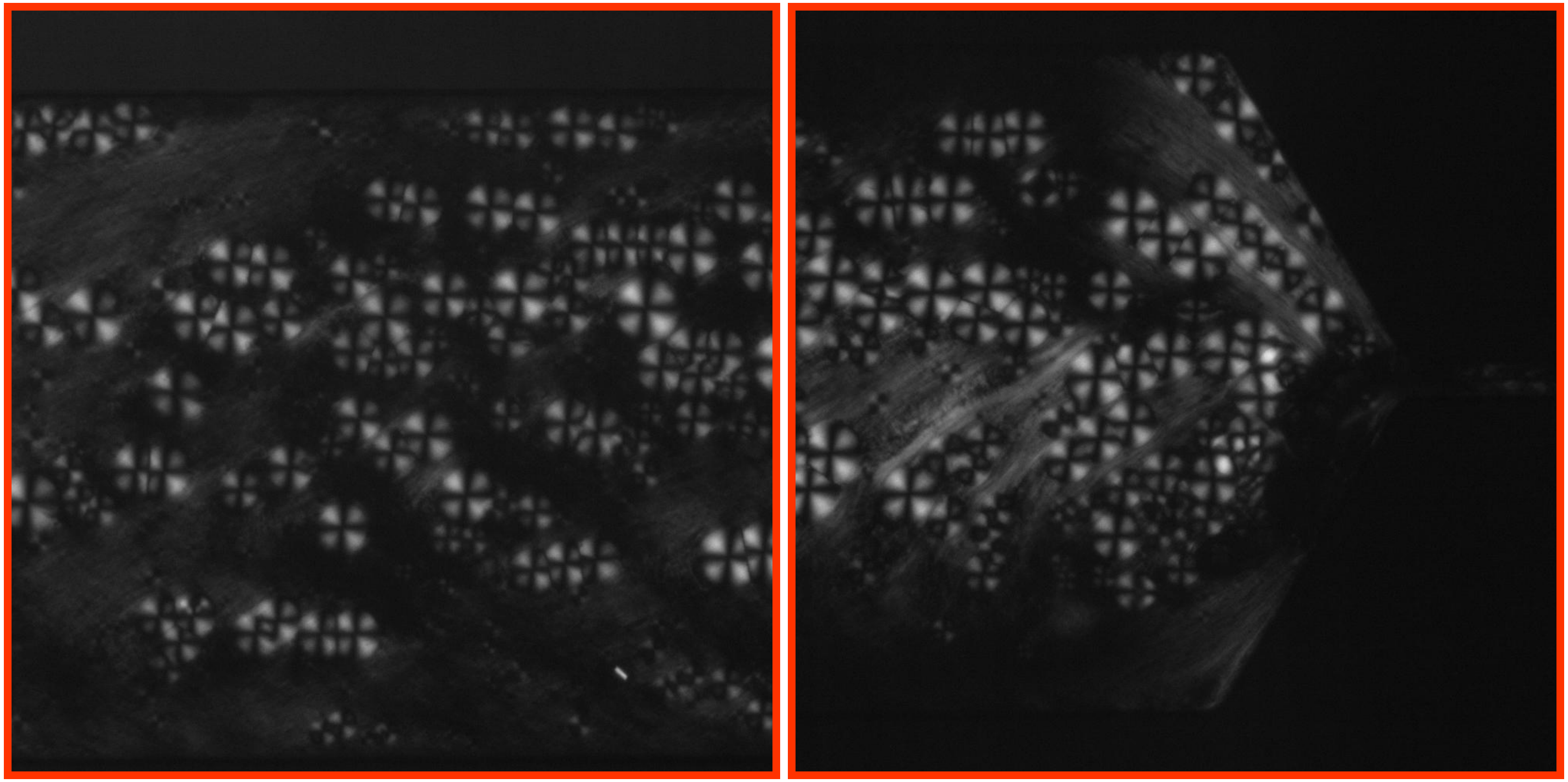
## CTAC/ Pentanol/Water



# **Periodic constrictions:** contraction/expansion flows





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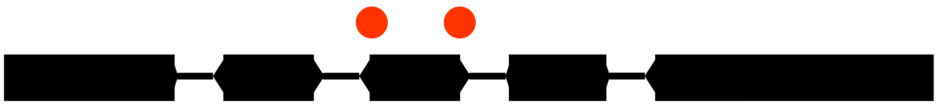

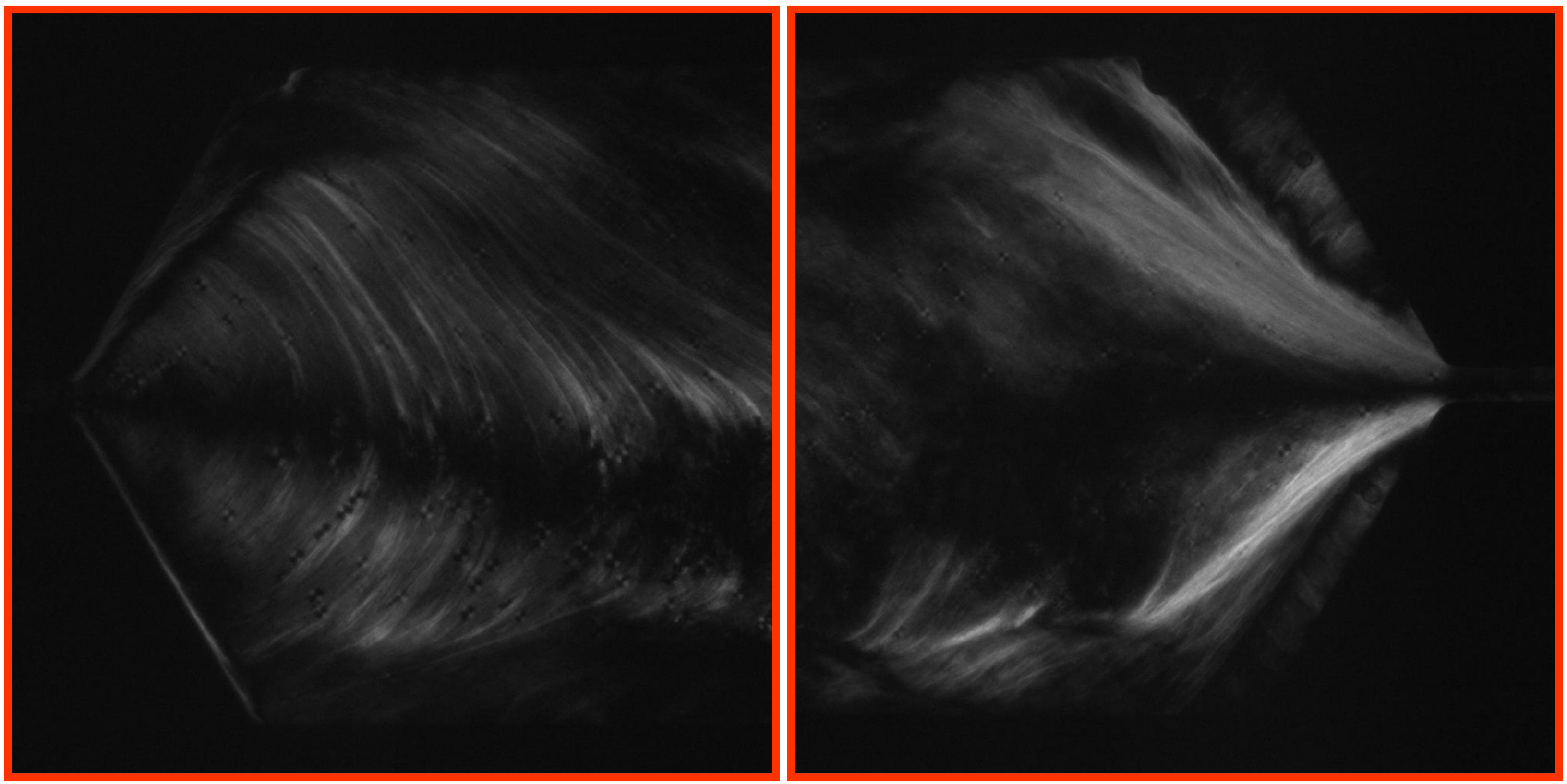

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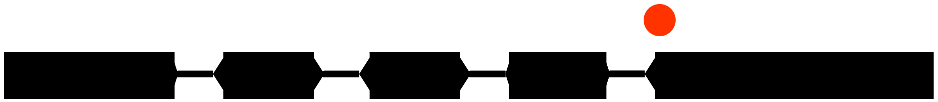

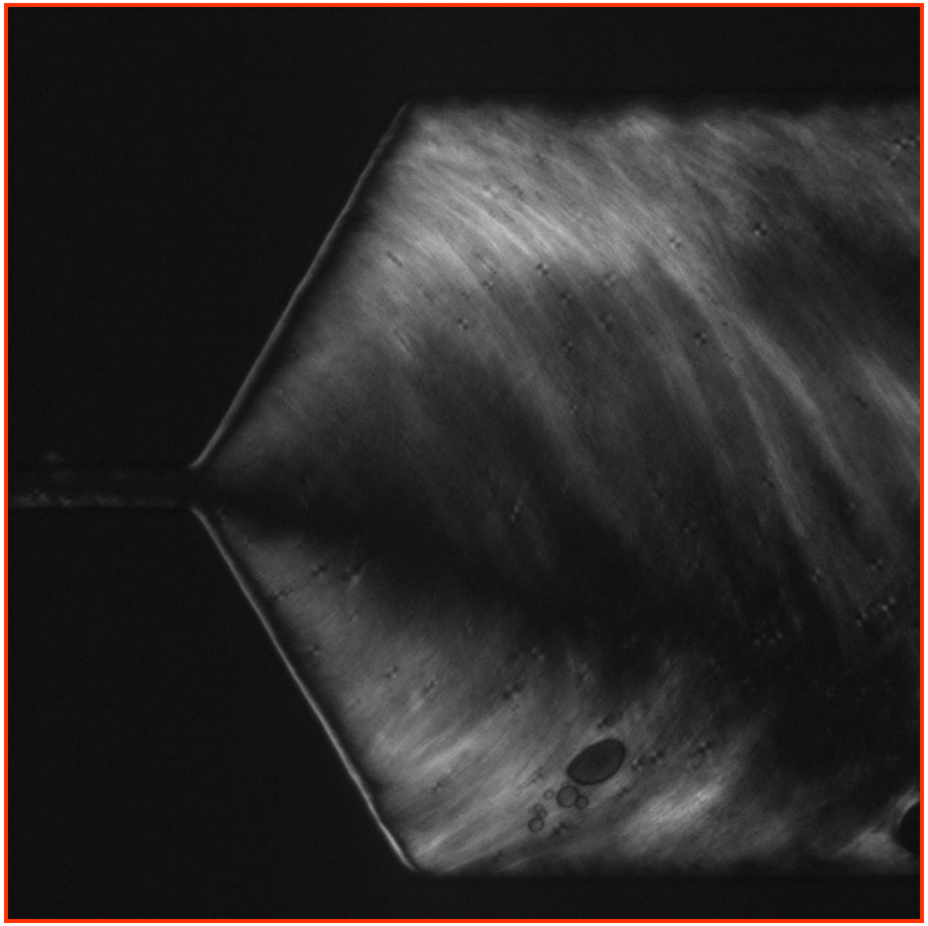

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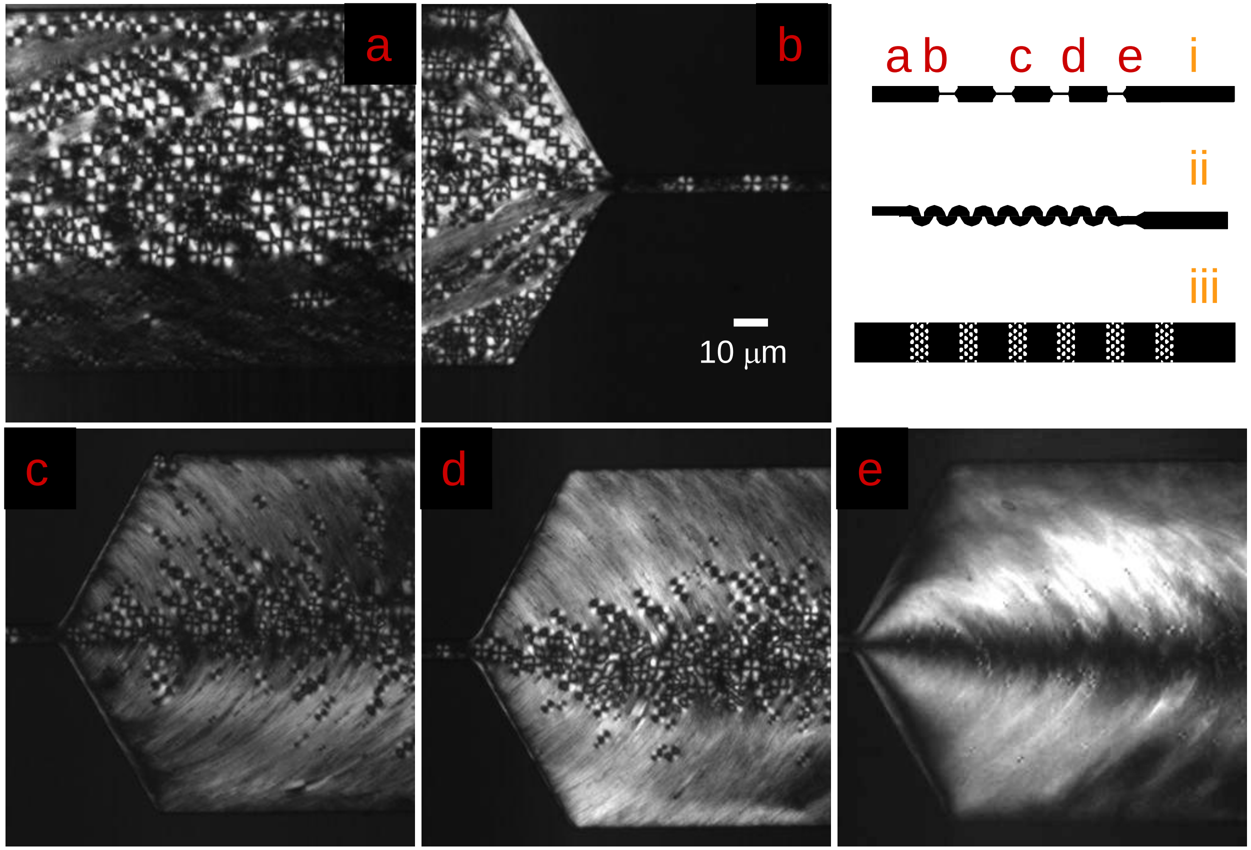
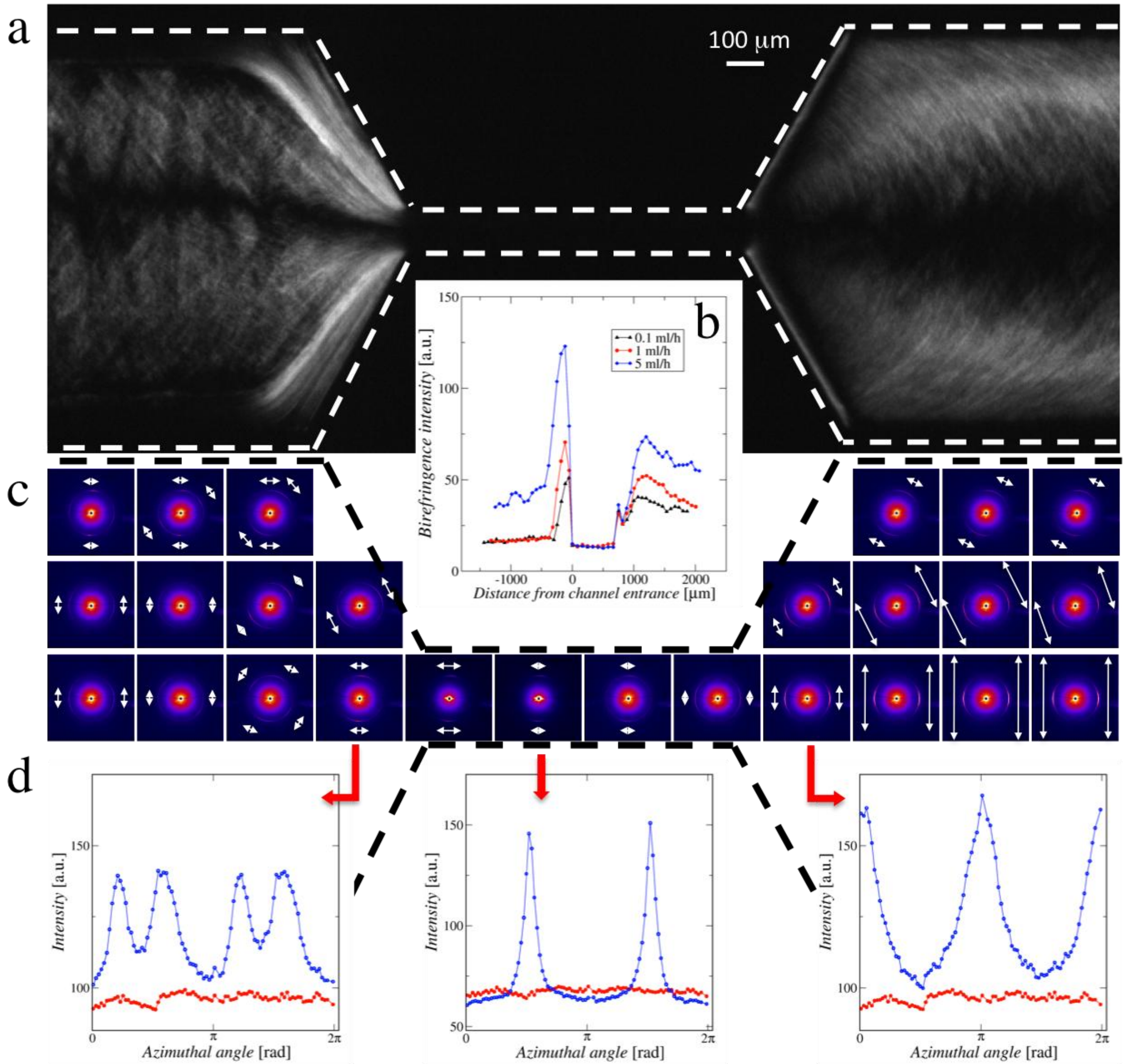



*Optical micrographs: mixture of SDS / Octanol / Brine*
*q= 1 ml/h; extension rate of $10^4$ $s^{-1}$.*

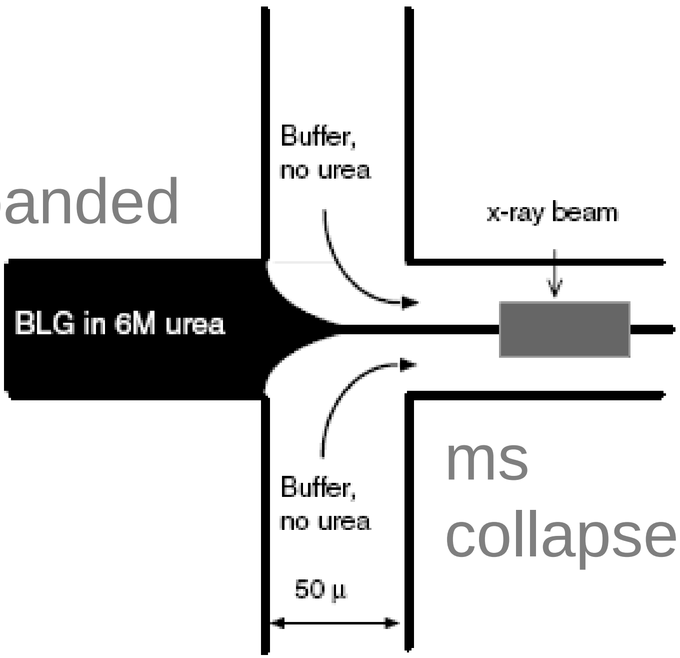
# Conclusion: *Microstructure alignment & orientation*



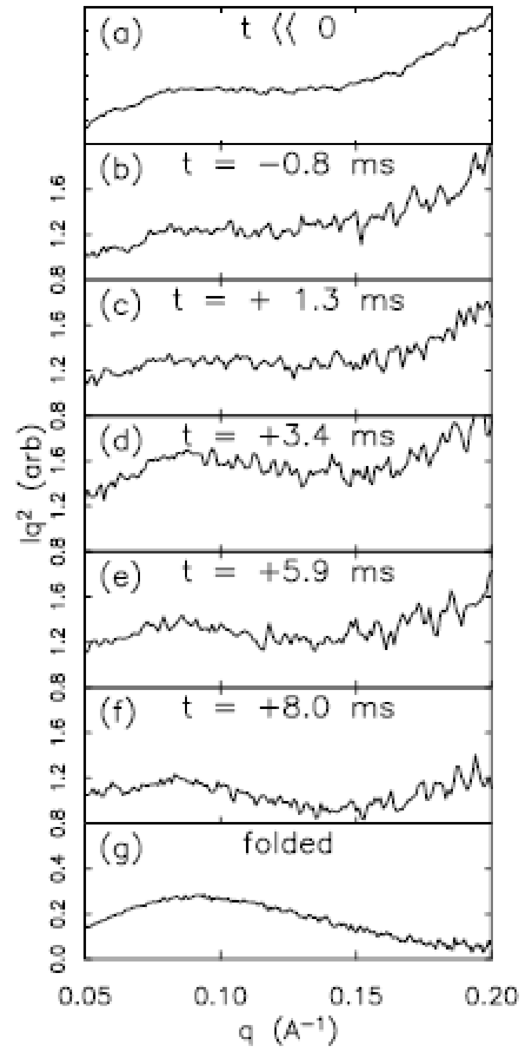
# Spatio-temporal mapping:

## Coil-to-globule transition

expanded




ms
collapse

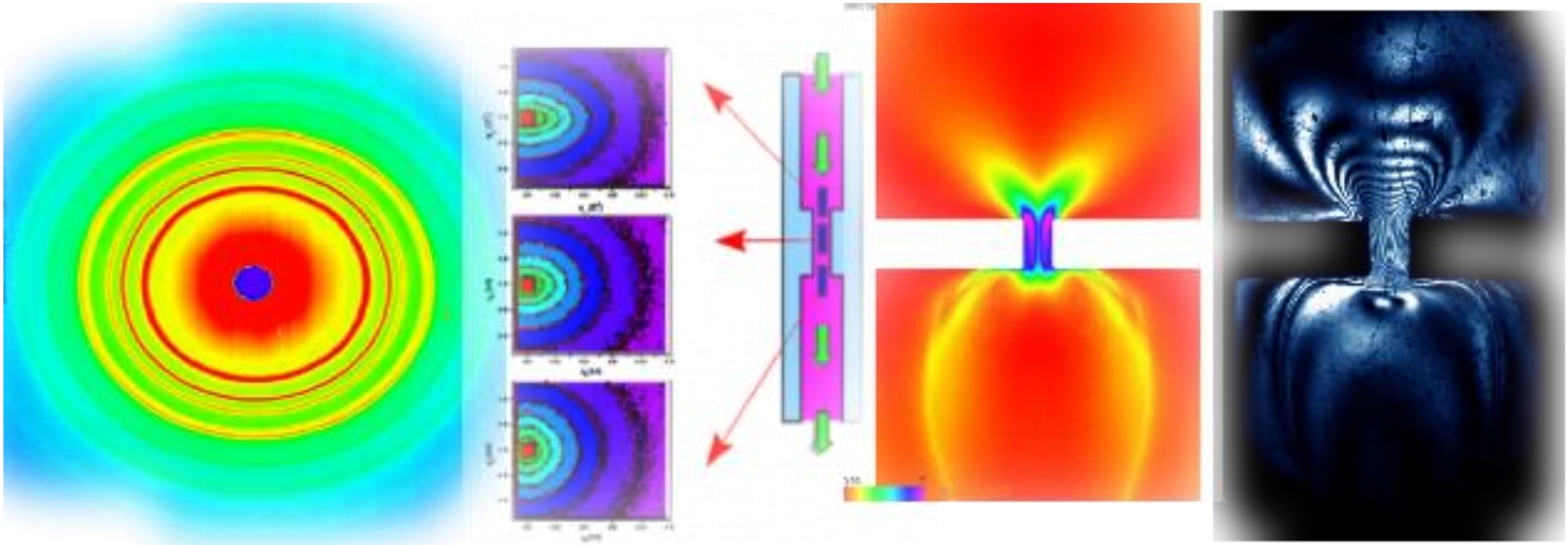



β-lactoglobulin (BLG)

(Pollack, Austin, etc)

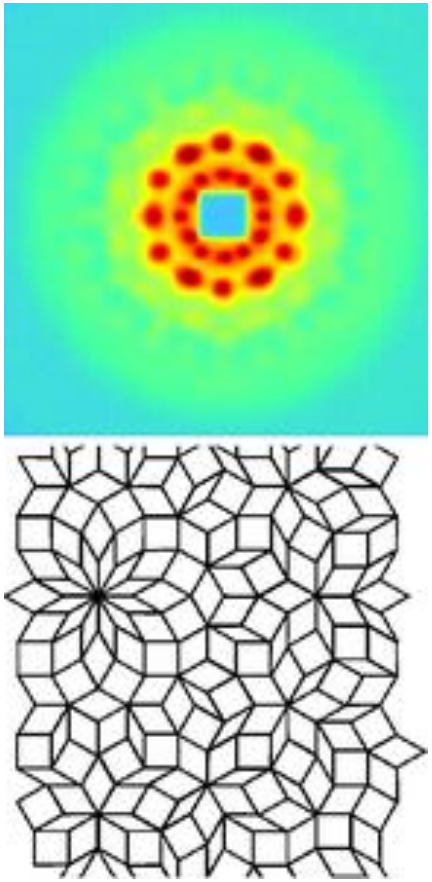
# Spatio-temporal mapping:

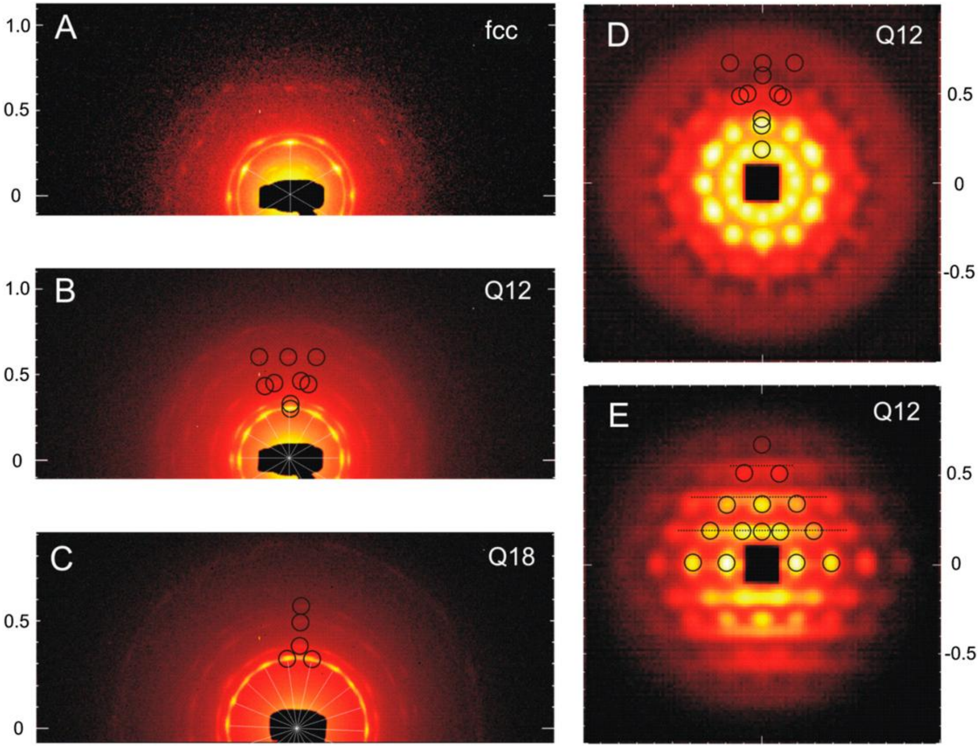
Entangled polymers under flow



Neutron-Mapping Polymer Flow: Scattering, Flow Visualization, and Molecular Theory
J. Bent, *et al.*
*Science* 301, 1691 (2003);

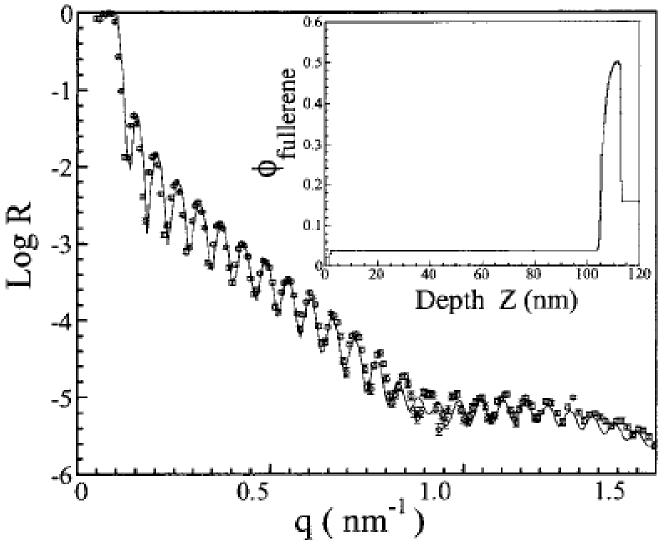
# Soft colloids under flow



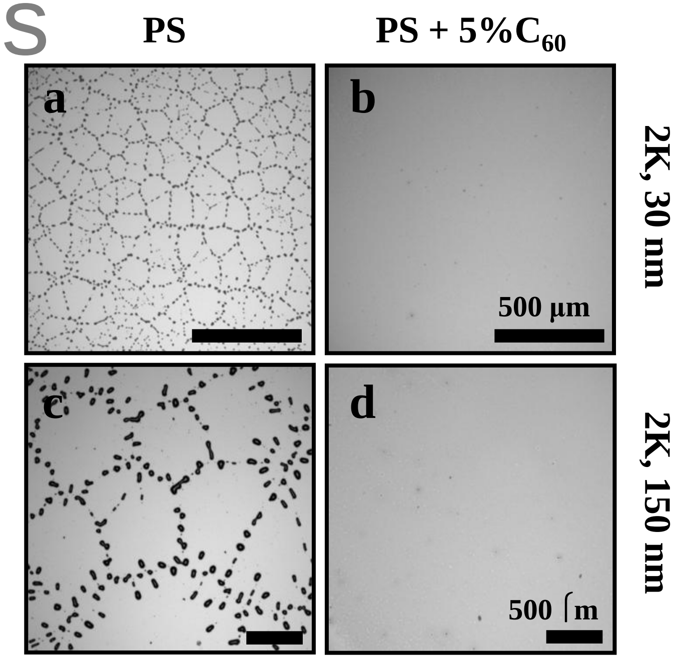



Forster et al. PNAS 2011

# Design 3D composites



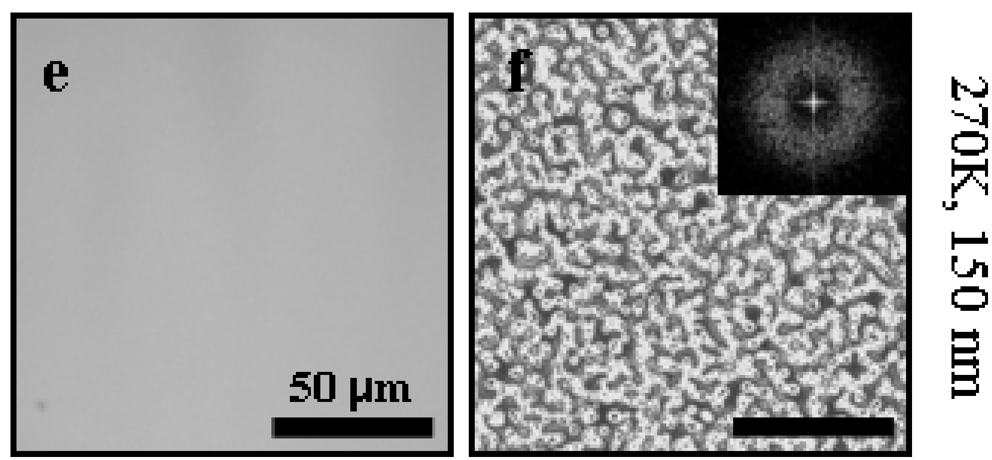

PS+5% C60 h = 100nm




140ºC

180ºC

GISANS & reflecometry




180ºC

PRL 2010

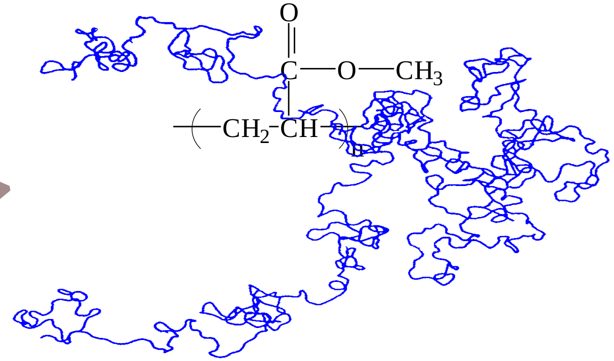
'Spinodal Clustering'

# Summary

1 **Intro**

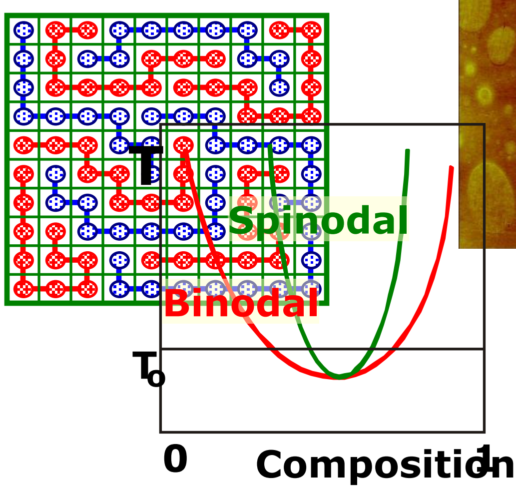
History

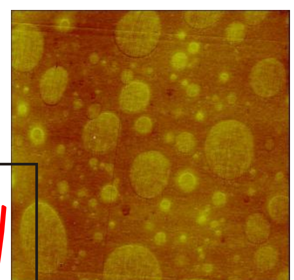
2 Soft matter




3 Form and structure

4 Mixtures & design



5 Outlook