

Neutrons in soft matter

Lecture 1 - Structure

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Outline

Lecture 1 – Structure & kinetics – SANS

Introduction

soft matter & relevance of neutron scattering

Single objects: spheres, coils, rods...

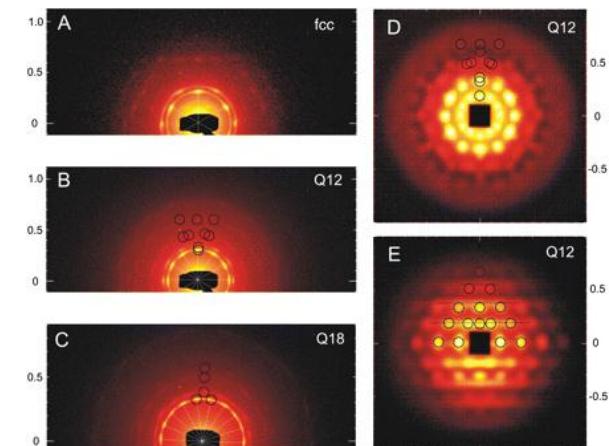
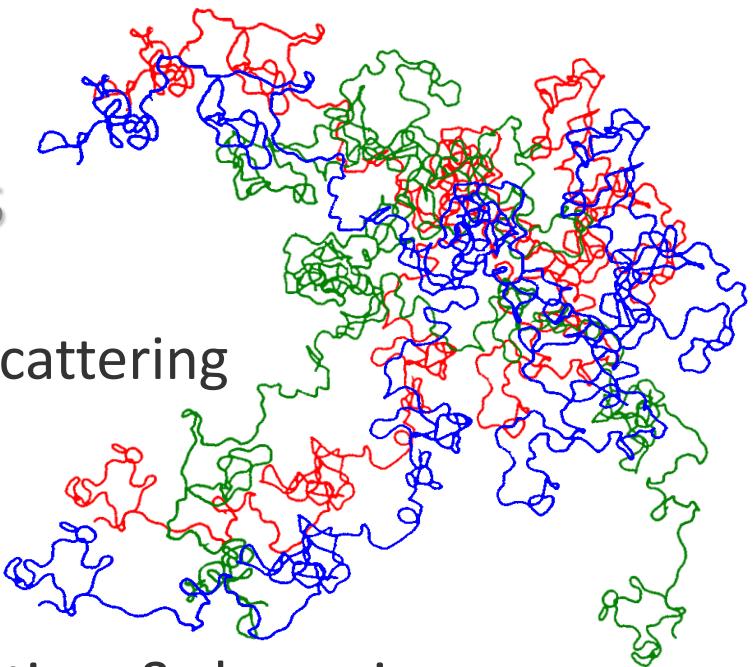
Single chain polymer conformation
(solution and blends)

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



Soft Matter

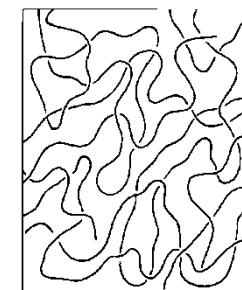
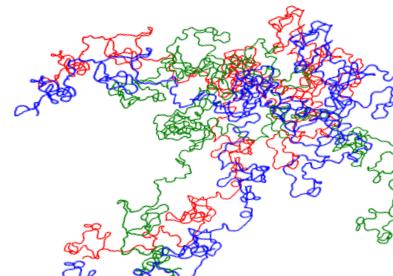
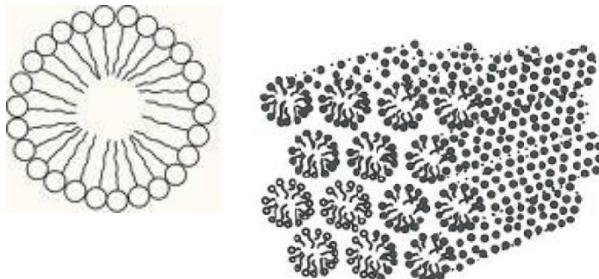
“molecular systems giving a strong response to very weak command signal”

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



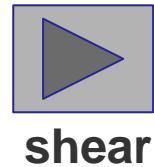
deGennes (1991)

Relevant energy scale comparable with room temperature thermal energy.



Sir Sam Edwards (-2015)

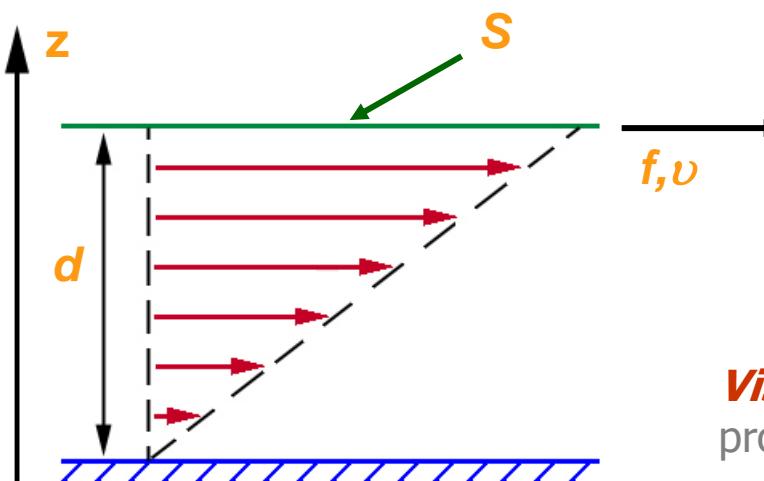
Complex fluids: including colloids, polymers, surfactants, foams, gels, liquid crystals, granular and biological materials.



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

Viscosity

Simplest setup
to measure
viscosity

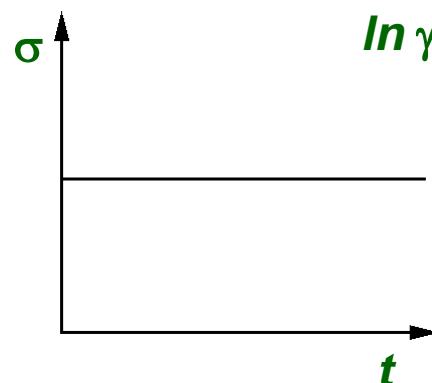


$$f = \eta \frac{Sv}{d}$$

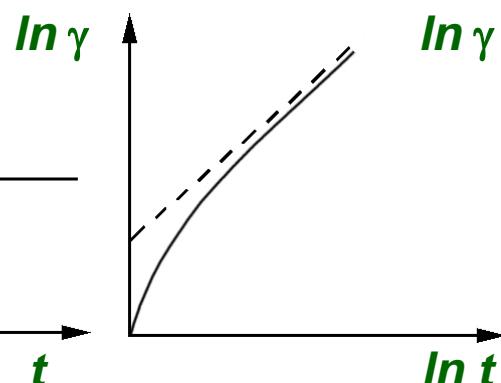
$$\sigma = \frac{f}{S} = \eta \frac{dv}{dz}$$

Viscosity:
proportionality coefficient η

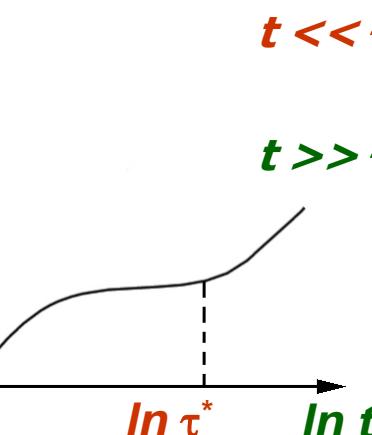
Viscoelasticity?



Step-wise stress
starting at $t=0$



normal liquid



polymer

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

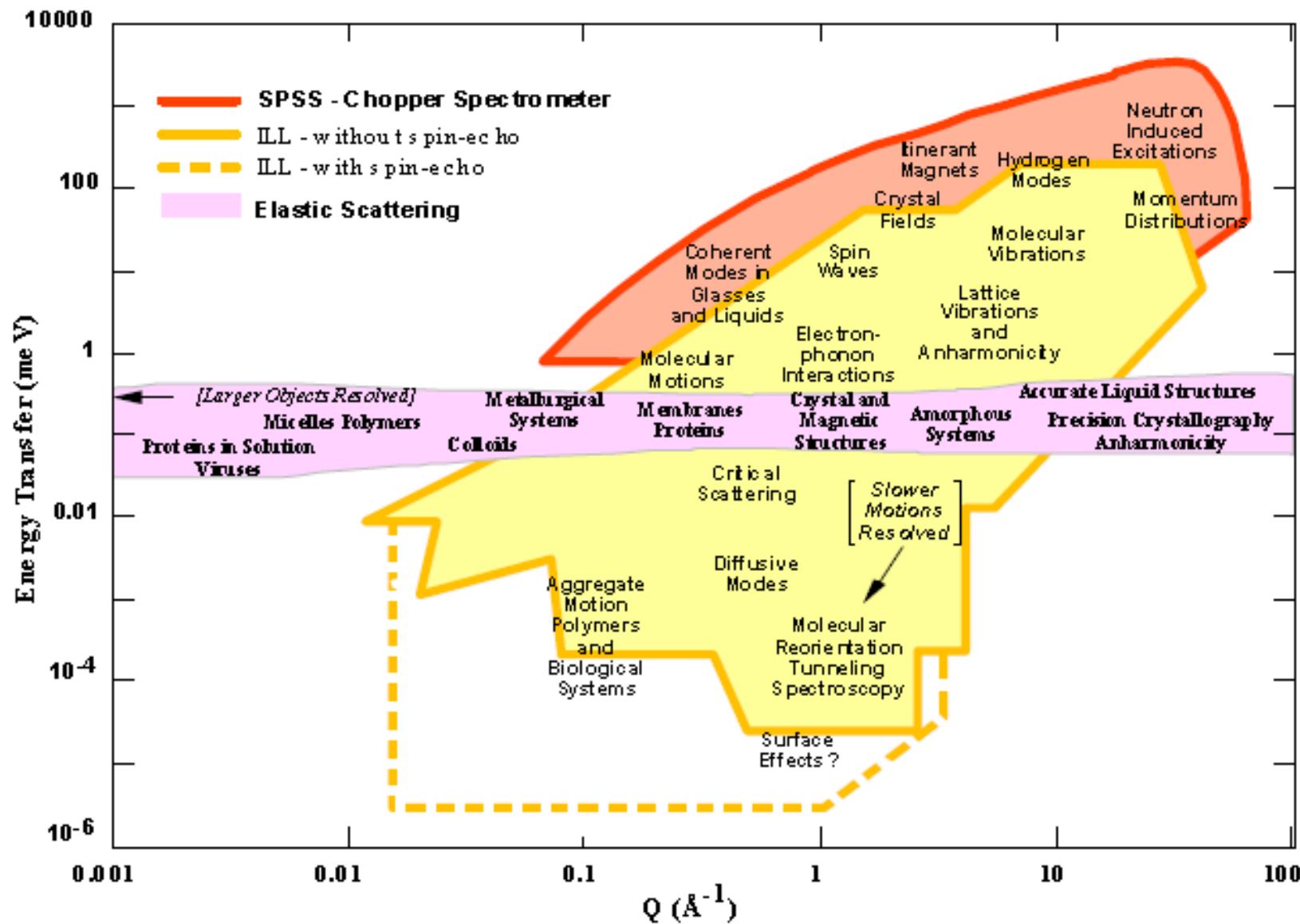
$$\gamma \approx \sigma/E$$

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

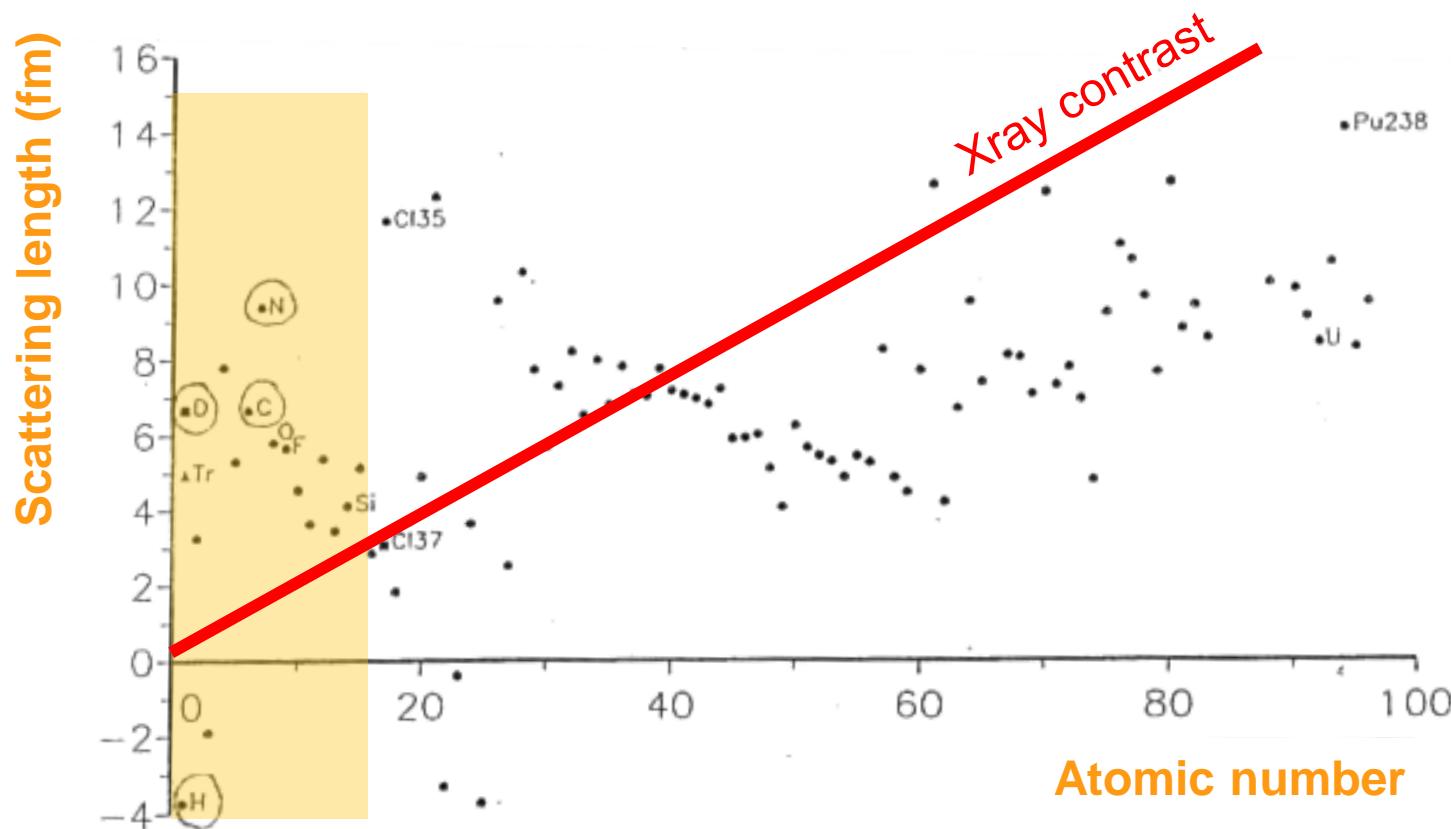
$$\gamma \propto \sigma \cdot t / \eta$$

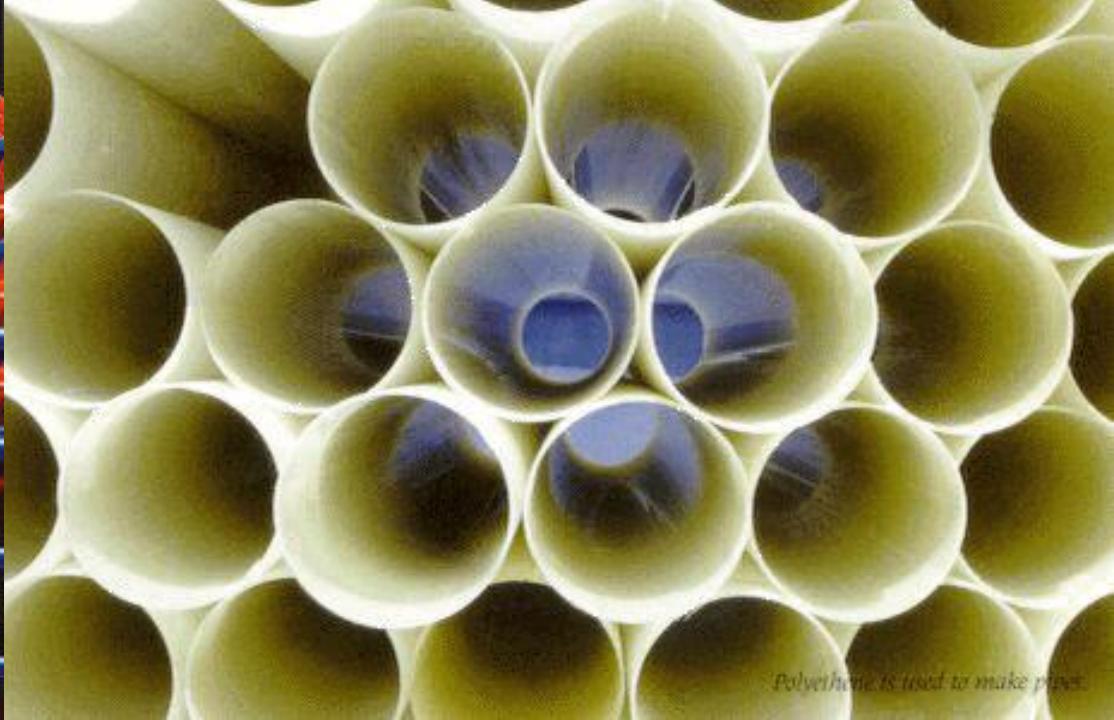
γ shear
angle

Neutron scattering is key in soft condensed matter



Neutron scattering is key in soft condensed matter





Polyethylene is used to make pipes

Common soft matter



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



Speciality polymers



Polymer key properties

Molecular weight, N



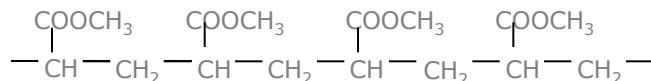
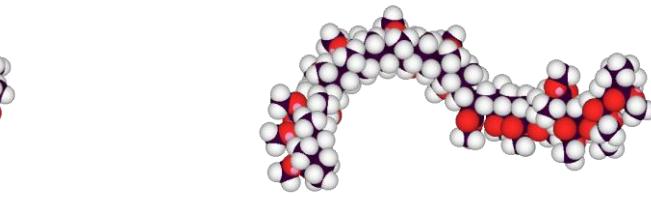
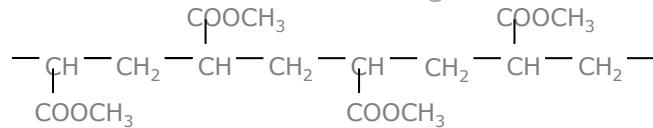
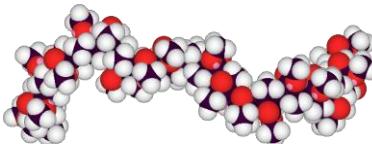
(size)

Polydispersity



(distribution of sizes)

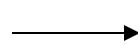
Tacticity



Glass transition (solid-liquid)

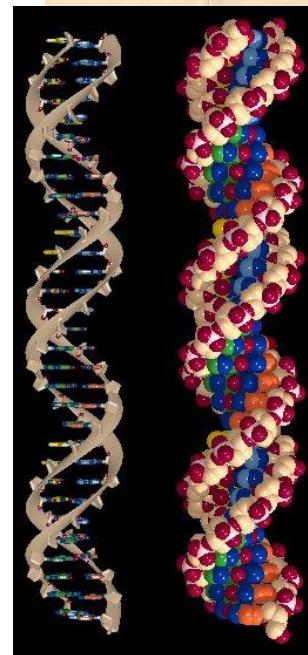
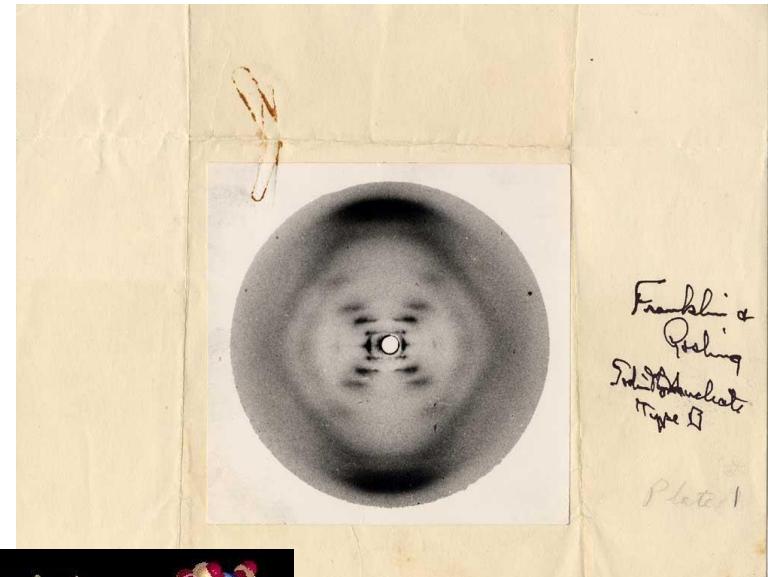
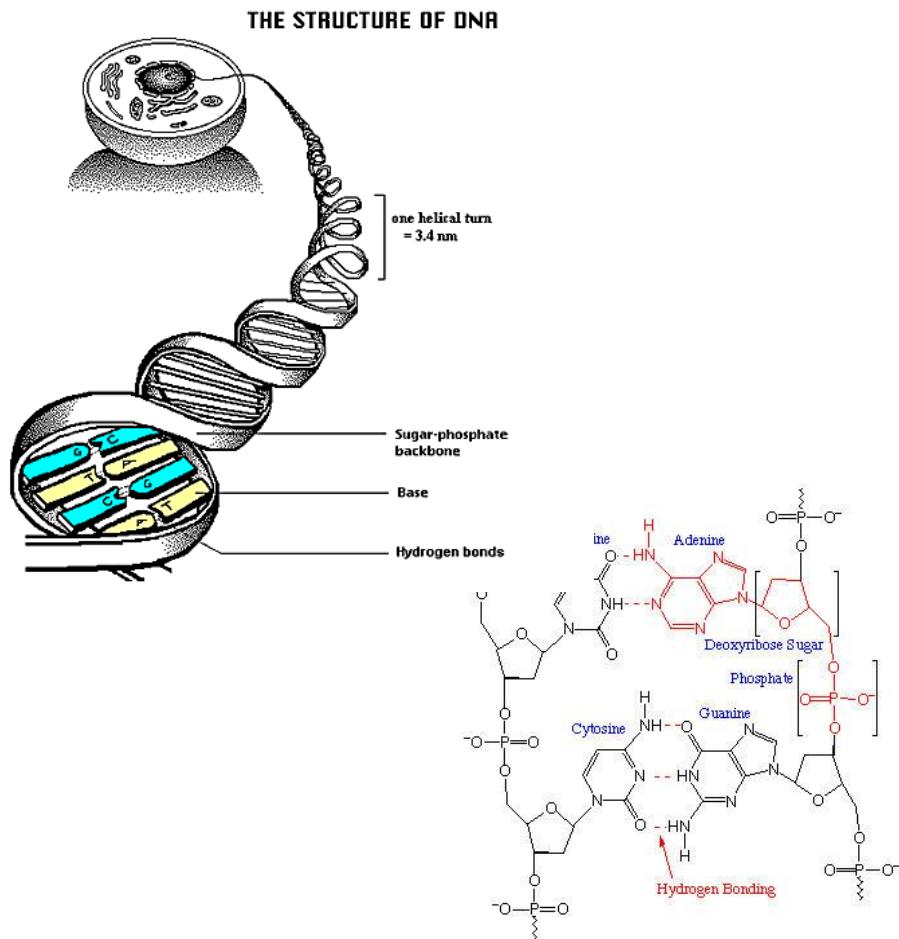
Crystallinity

Interaction parameter χ

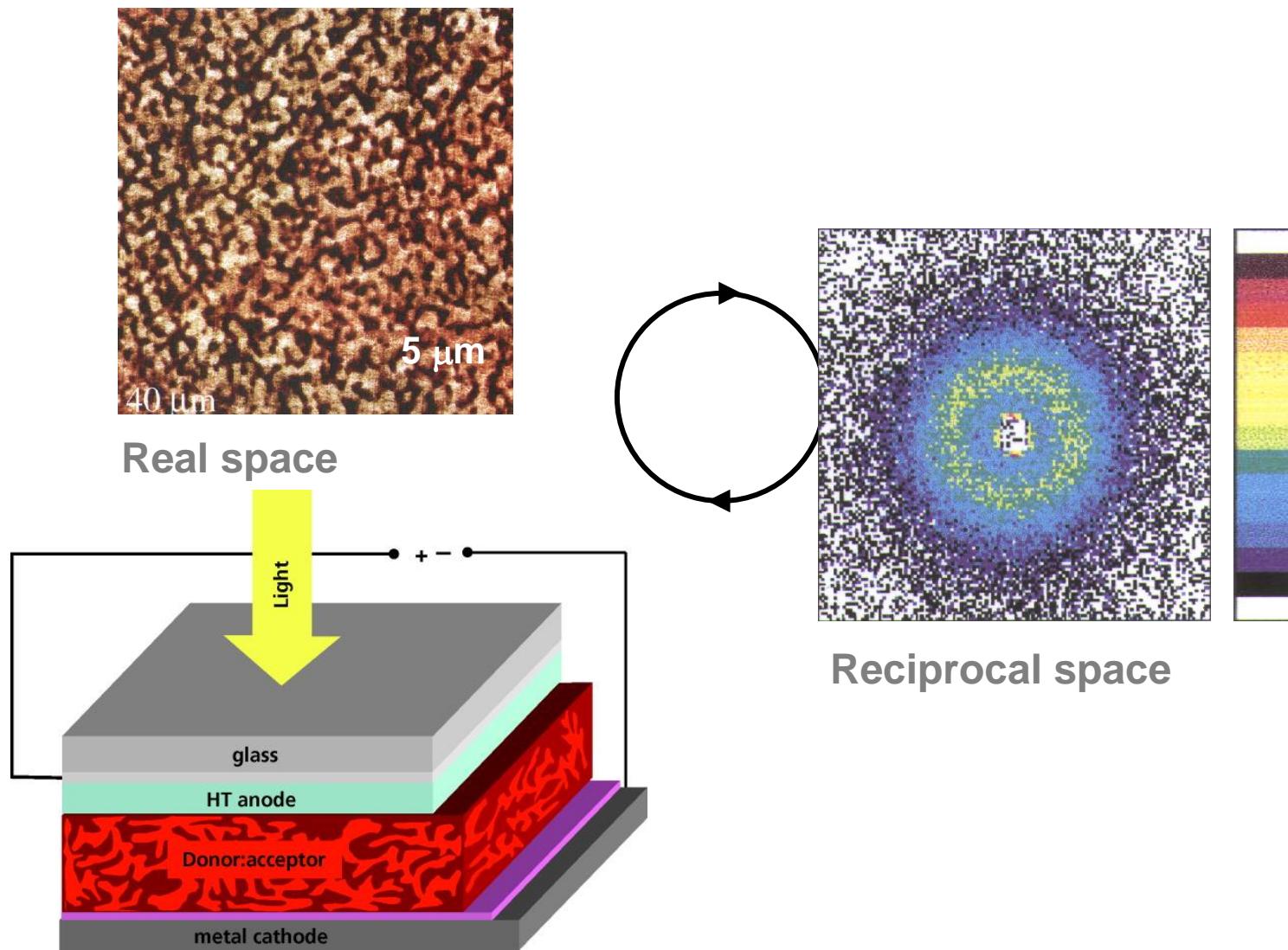


Combine properties to make new materials!

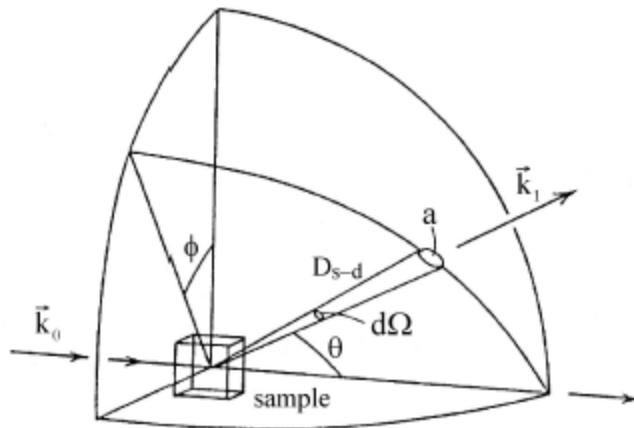
Soft matter: DNA



Soft Matter: membranes, photovoltaics (BHJ)



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

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

Dynamic structure factor

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

Intermediate scattering function

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

Pair correlation function

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

$$\int d\omega$$

$$\rightarrow$$

Elastic structure factor

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

$$S(\mathbf{q})$$

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

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

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

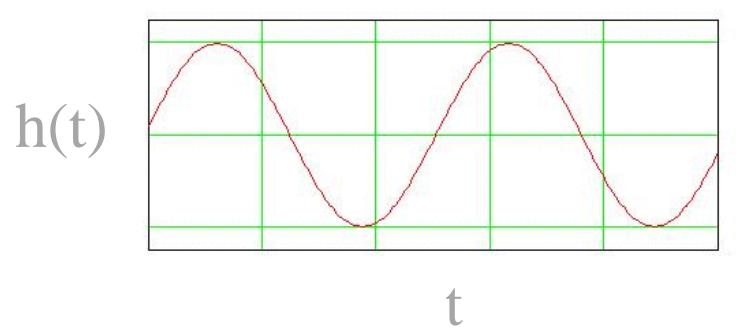
$$h(t) = \int_{-\infty}^{\infty} H(f) e^{-2\pi i f t} df$$



Fourier
transform:

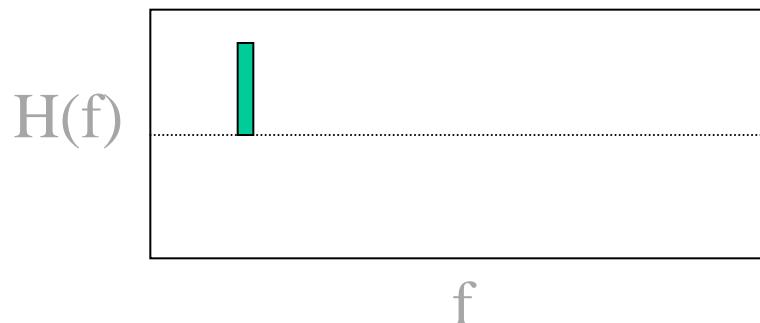
$$\Phi(H(f), t) = h(t)$$

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



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

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



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

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

Reminder: Fourier Transforms

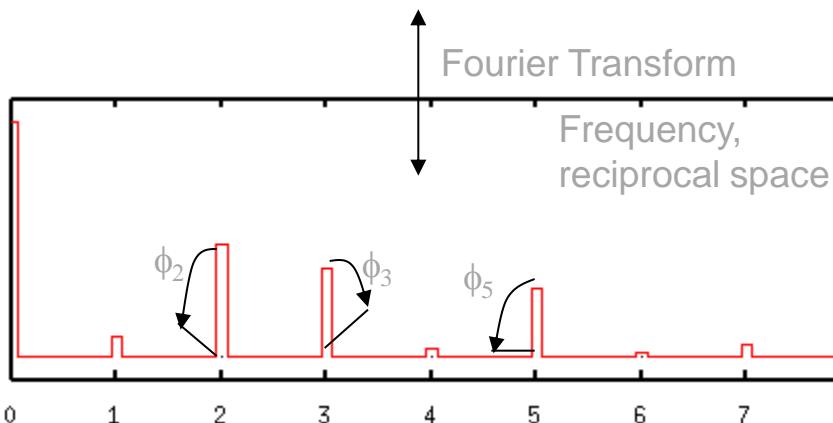
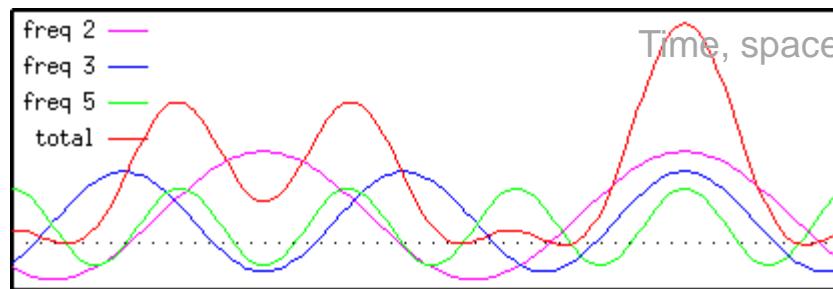
$$H(f) = \int_{-\infty}^{\infty} h(t) e^{2\pi i f t} dt$$

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

Fourier transform:

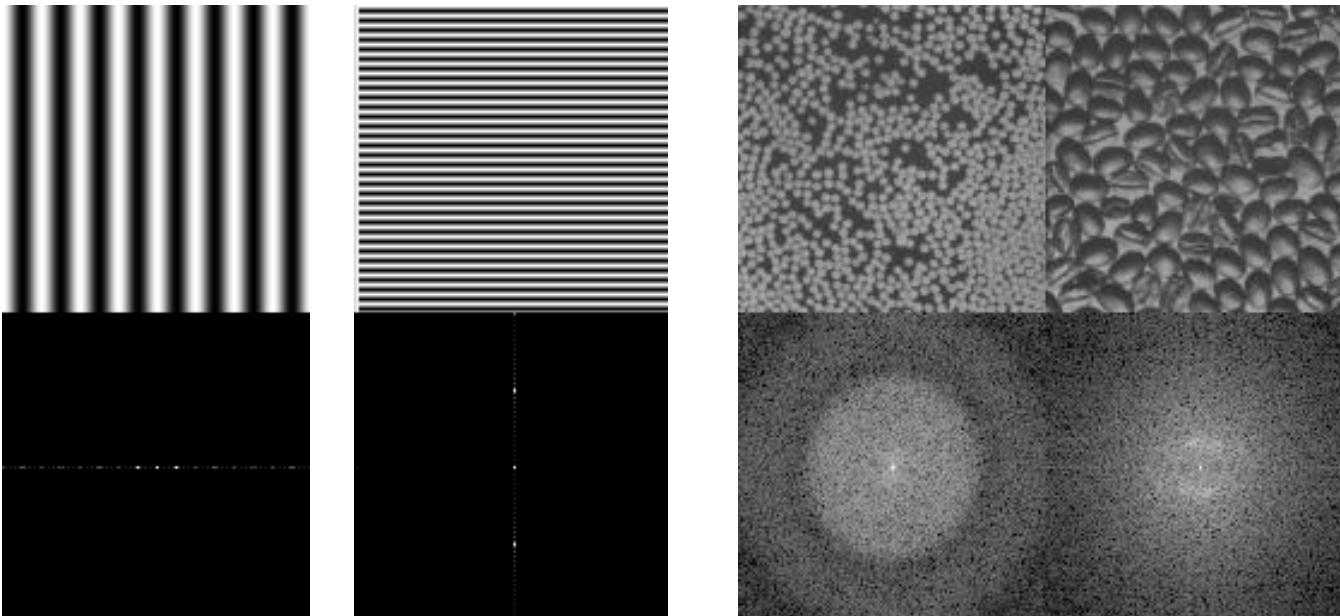
$$\Phi(H(f), t) = h(t)$$

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



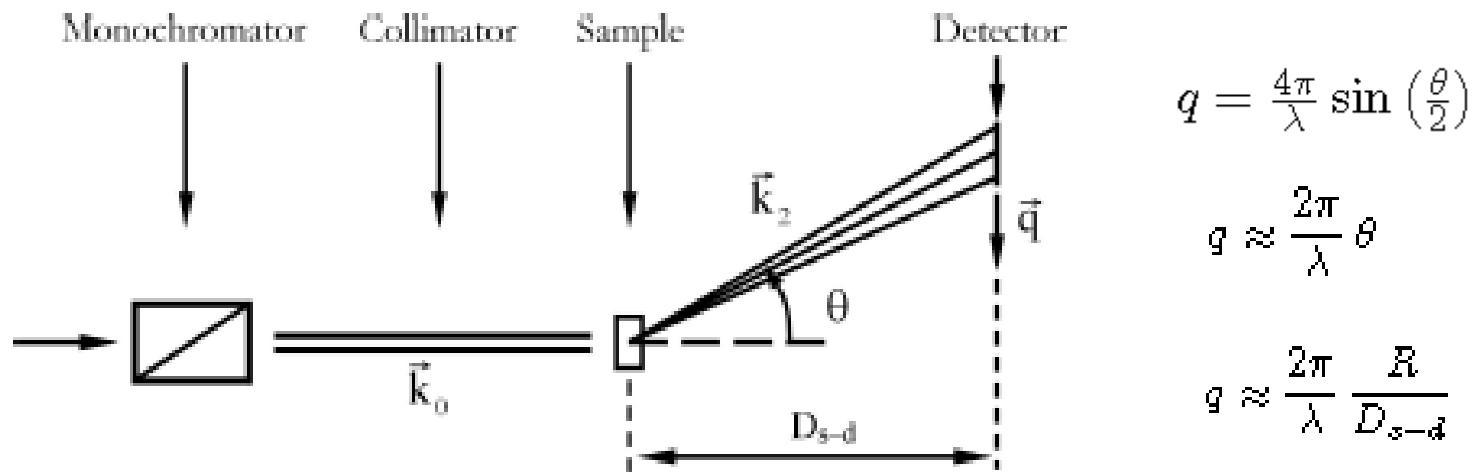
Reminder: Fourier Transforms

Real space



Reciprocal space

SMALL-ANGLE NEUTRON SCATTERING



Absolute scattering intensity [cm⁻¹]

$$\frac{\partial \sigma}{\partial \Omega}(Q) = N_p V_p^2 (\Delta \delta)^2 P(Q) S(Q) + B_{in} \quad \text{incoherent background}$$

number density / volume / contrast

form factor | structure factor

Scattering length density

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

Relationship between q λ θ and d

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

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

small $q \sim$ large d [large $q \sim$ small d]
small $\lambda \sim$ large $q \sim$ small d
[large $\lambda \sim$ small $q \sim$ large d]

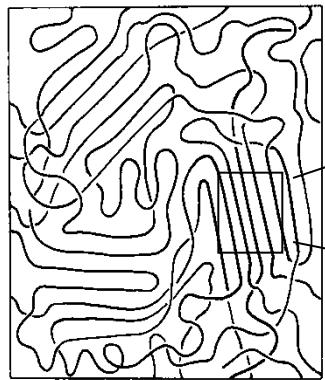
Radiation	Wavelength
light	~ 500 nm
X-rays	~ 1 Å
neutrons	~ 5 Å

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

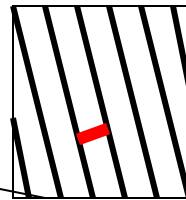
Bottom line:

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 $d \sim 20$
nm
 $q = 2\pi/d \sim 0.3 \text{ nm}^{-1}$

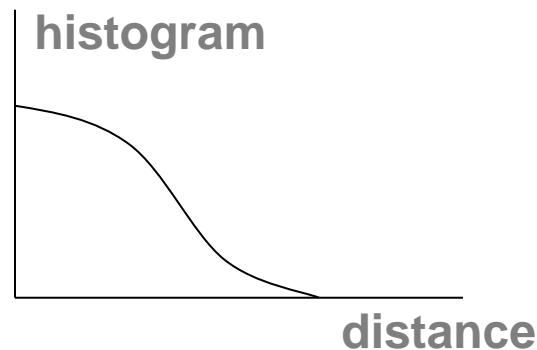
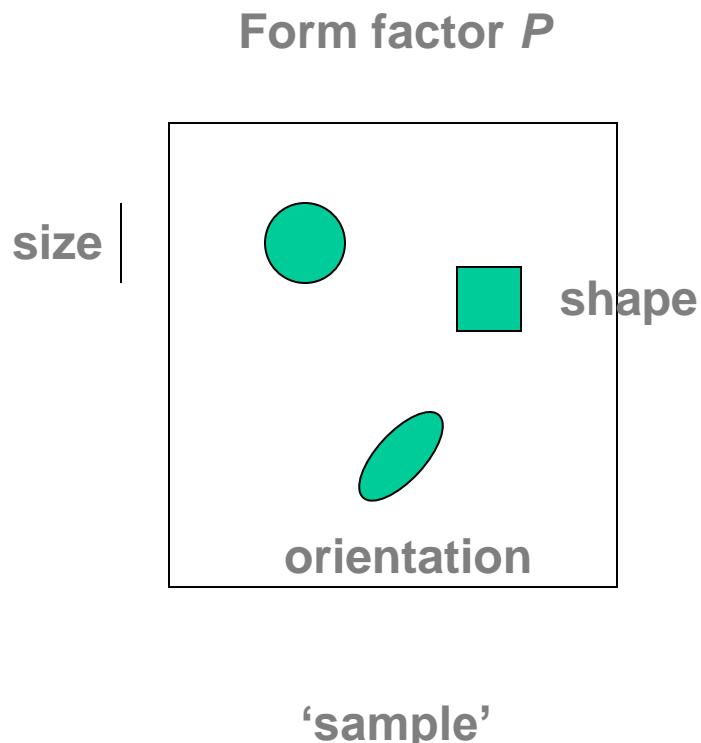
$$q = \frac{4\pi}{\lambda} \sin(\theta/2)$$

Radiation	Wavelength	Scattering angle
X-rays	$\sim 1 \text{ \AA}$	$\theta \sim 0.27 \text{ degrees}$
neutrons	$\sim 5 \text{ \AA}$	$\sin(\theta/2) \sim 0.013, \theta \sim 0.7 \text{ degrees}$
light	$\sim 500 \text{ nm}$	$\sin(\theta/2) > 1$ impossible!

the smallest dimension probed by wavelength λ corresponds to largest angle $\theta=180$ degrees (backscattering). For light $d_{min} \sim 0.25 \mu\text{m}$, for X-rays or neutrons $d_{min} \sim 0.5$ to 2.5 \AA .
In typical experiments, scattering angles range from $0.1 < \theta < 70$ degrees

Form factor: P

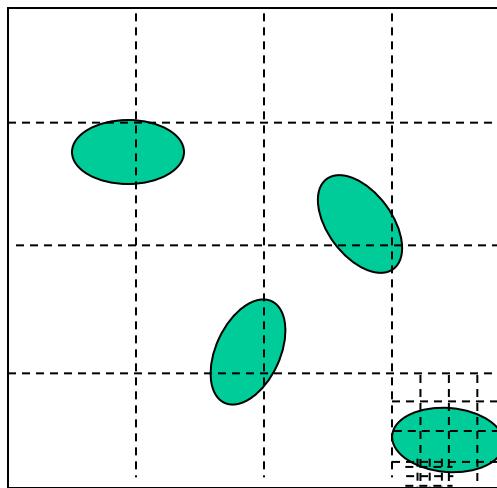
Self-correlations



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

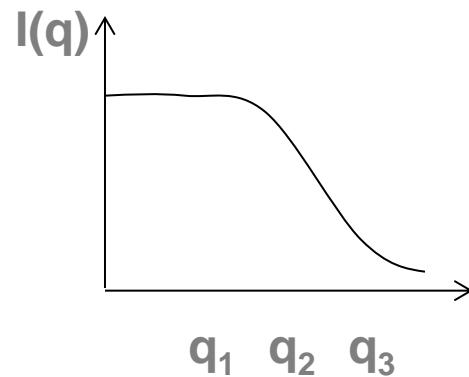
Interference between scattered radiation
from different parts of the same object
(analytical solutions for common shapes)

Multiple lengthscales



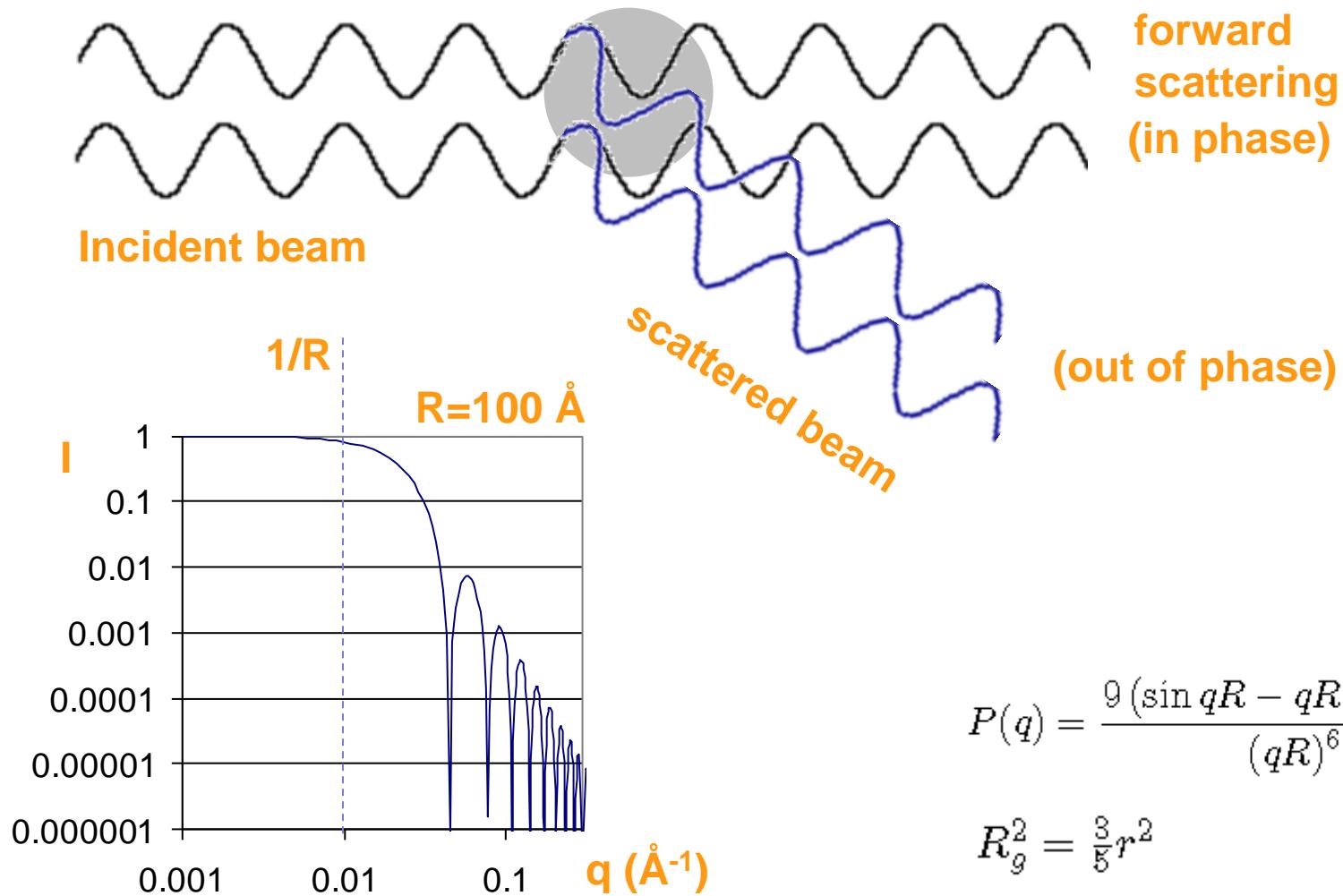
$2\pi/q_3 \quad 2\pi/q_2$

$2\pi/q_1$

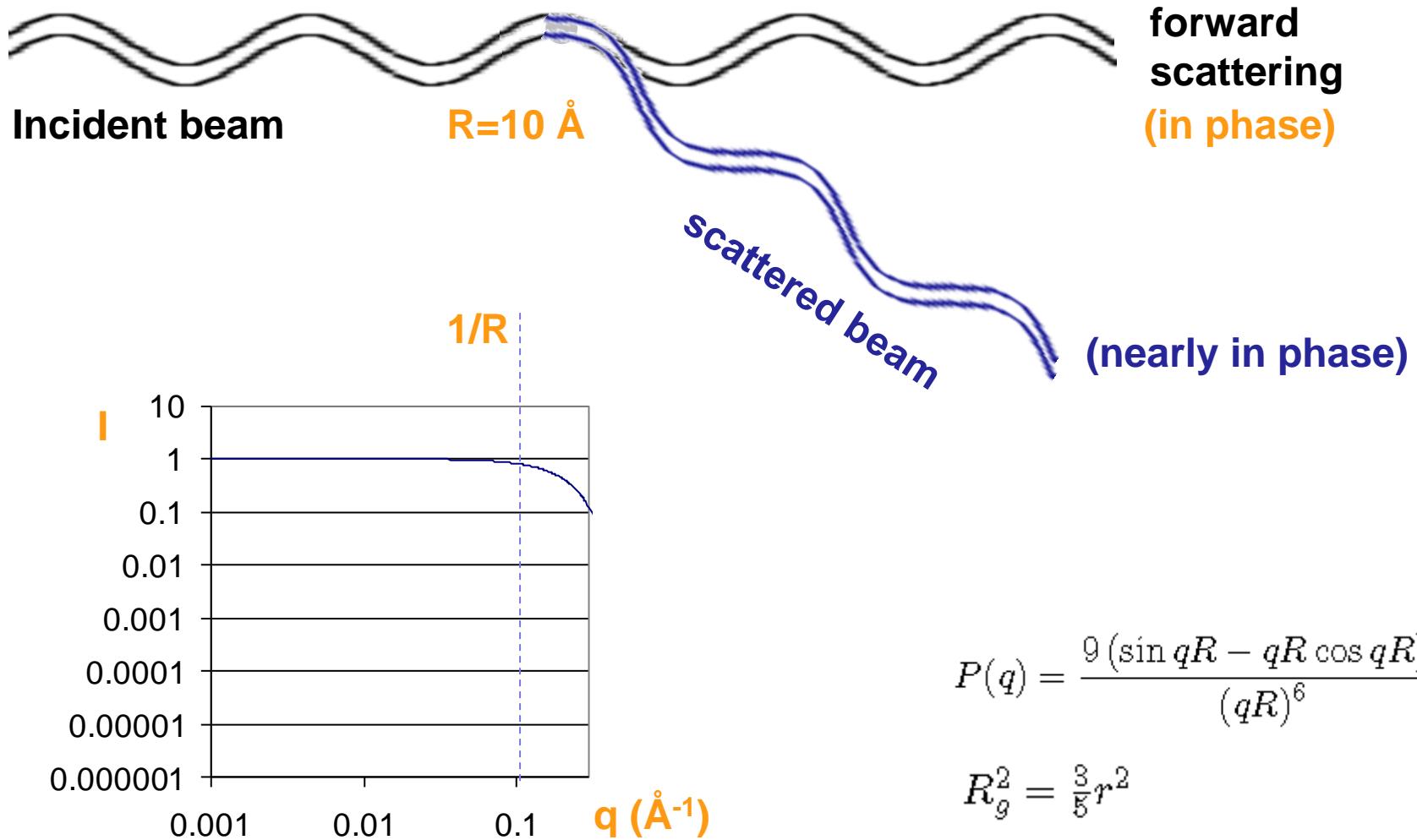


scattering spectrum corresponds to different “magnifications”, thus several approximations may be relevant

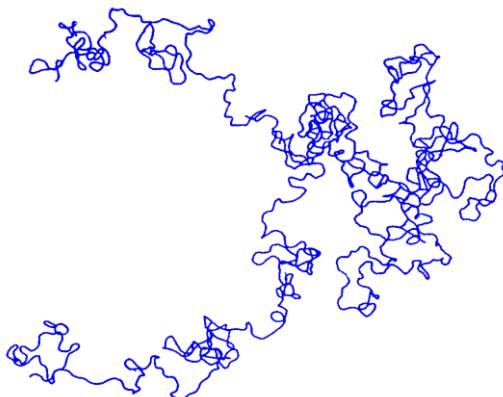
Scattering from a sphere



Scattering from a (tiny) sphere



Scattering from a random coil



Debye form factor

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

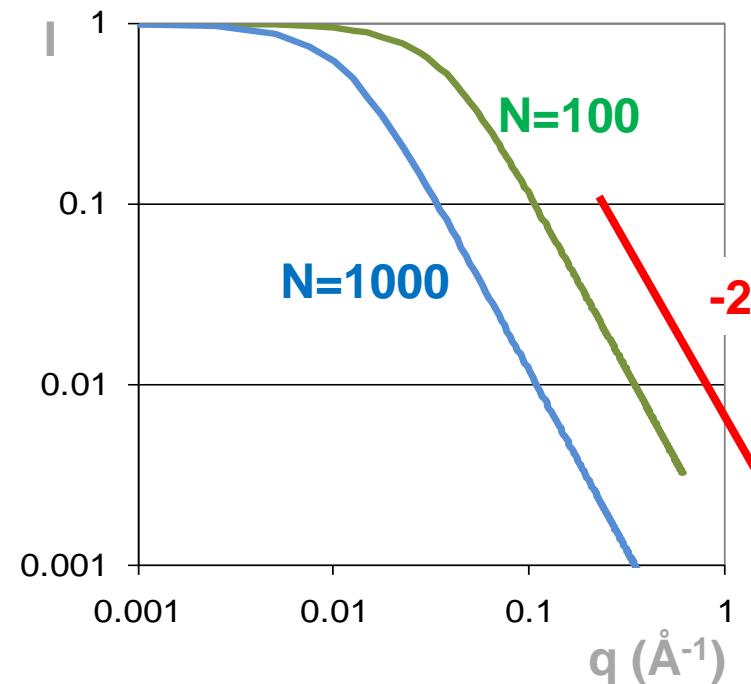
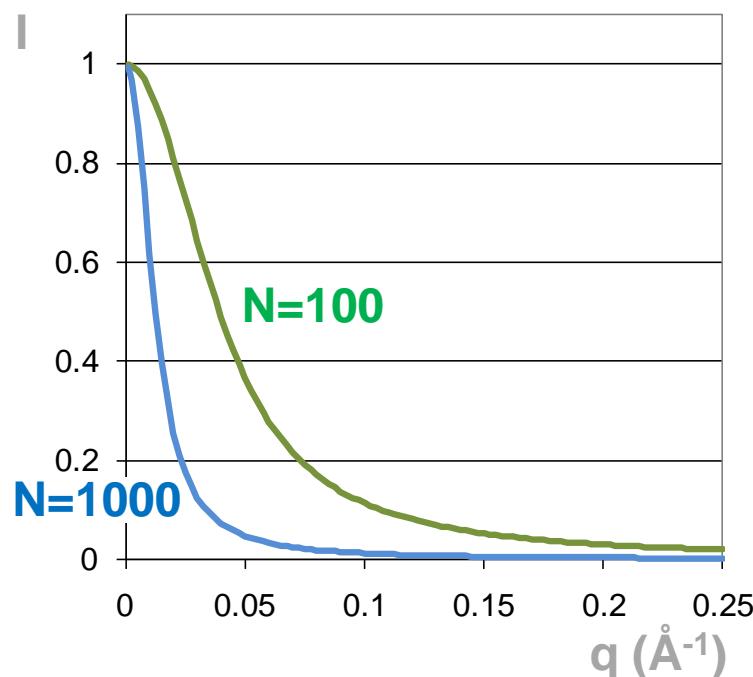
$$x \equiv q^2 R_g^2$$

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

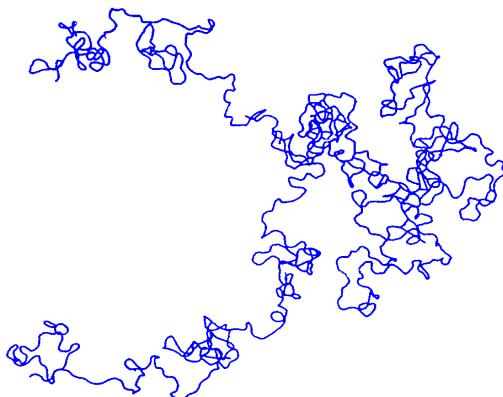
$a = 10 \text{ \AA}$

$N=100 \rightarrow R_g \approx 4 \text{ nm}$

$N=1000 \rightarrow R_g \approx 13 \text{ nm}$



Scattering from a random coil



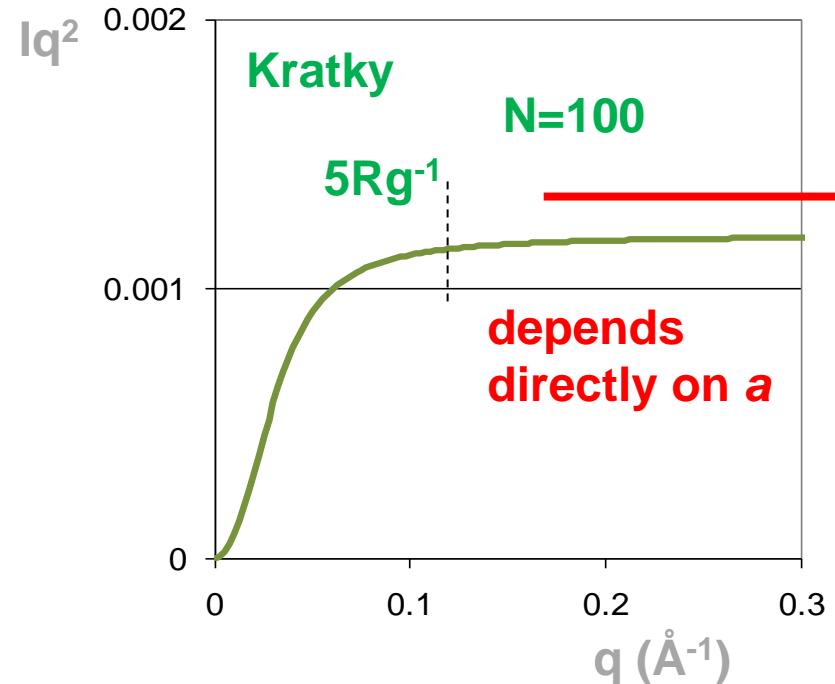
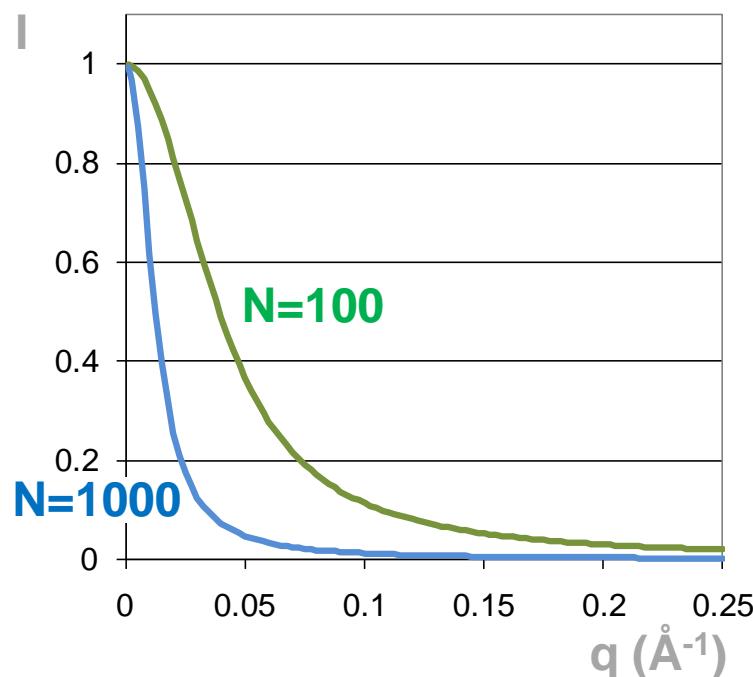
Debye form factor

$$g_D(x) = \frac{2}{x^2} (x - 1 + e^{-x})$$
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$$R_g^2 = \frac{Na^2}{6}$$

$a=10 \text{ \AA}$

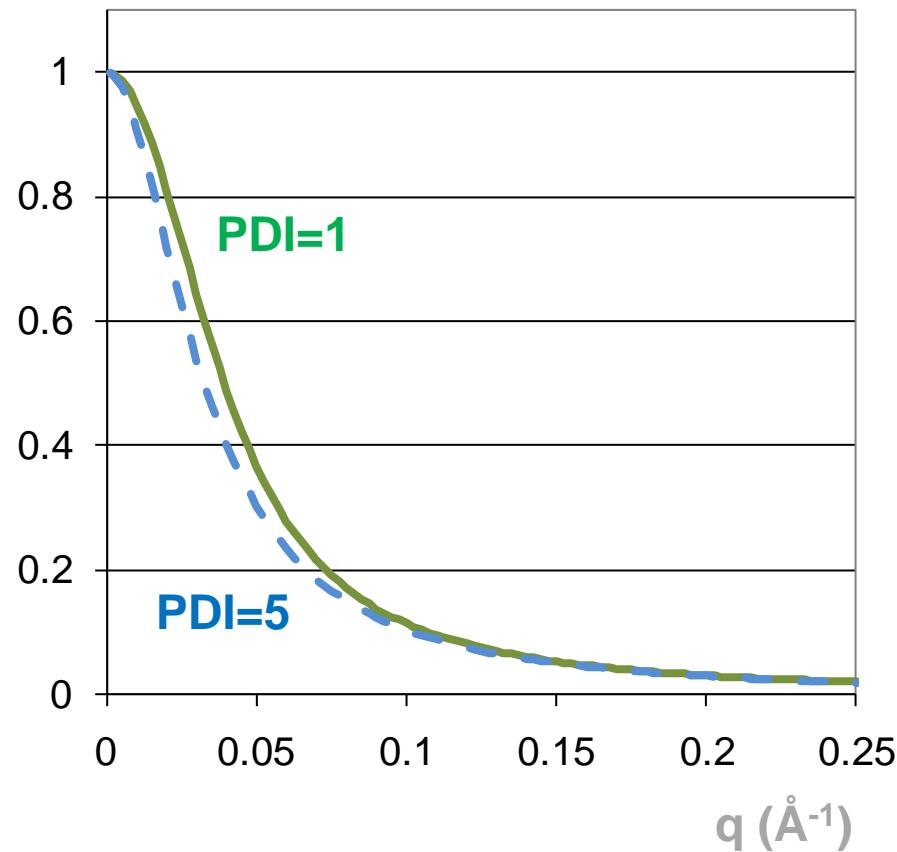
$N=100 \rightarrow R_g \approx 4 \text{ nm}$

$N=1000 \rightarrow R_g \approx 13 \text{ nm}$



Polydisperse random coils

$M_n/M_w \ g_D$



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)

$a=10 \text{ \AA}$

$N=100 \rightarrow Rg \approx 4 \text{ nm}$

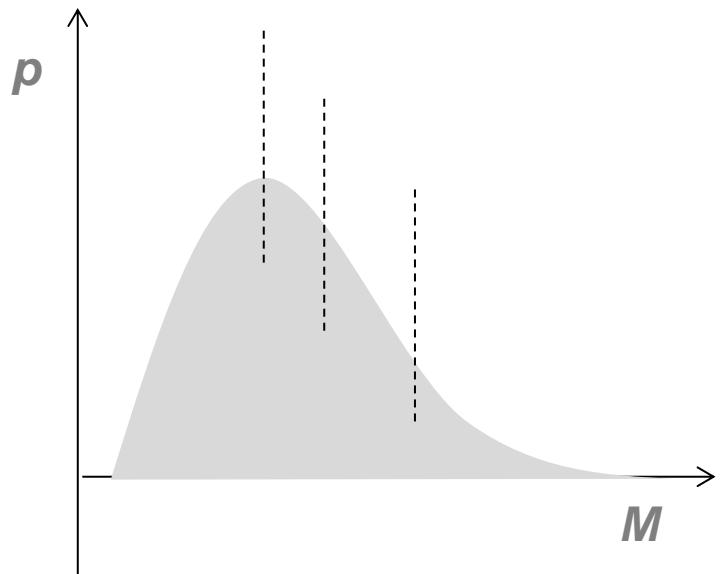
$N_w=100, N_w/N_n=5$

A polydispersity model

(Schultz-Zimm)

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

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

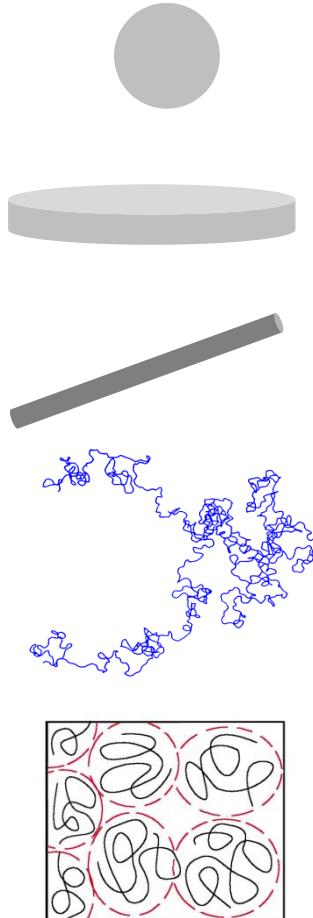


Number average $M_n = \int p(M) M dM$

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

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

Useful form factors

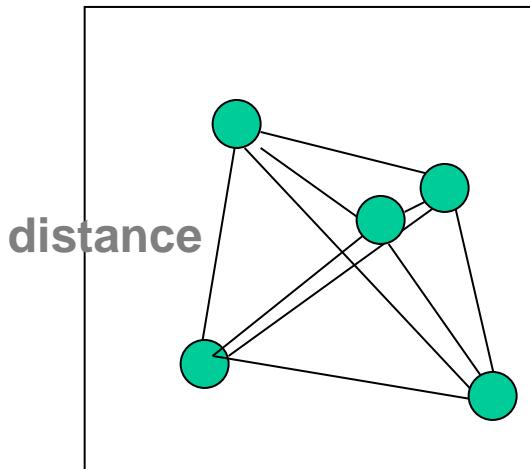


Sphere of radius R_p	$P(Q) = \left[\frac{3(\sin(QR_p) - QR_p \cos(QR_p))}{(QR_p)^3} \right]^2$
Disc of negligible thickness and radius R_p (J_1 is a first-order Bessel function)	$P(Q) = \frac{2}{(QR_p)^2} \left[1 - \frac{J_1(2QR_p)}{QR_p} \right]$
Rod of negligible cross-section and length L (S_i is 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 $U = \frac{(QR_g)^2}{(1+2Y)}$	$P(Q) = \frac{2[(1+UY)^{-\frac{1}{2}} + U - 1]}{(1+Y) U^2}$
Concentrated polymer solution with screening length ξ where $\xi = R_s \left(\frac{\phi}{\phi^*} \right)^{\frac{1}{1-\alpha}}$	$P(Q) = P(0) \left[\frac{1}{1 + (Q\xi)^2} \right]$

S King

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

Structure factor: S

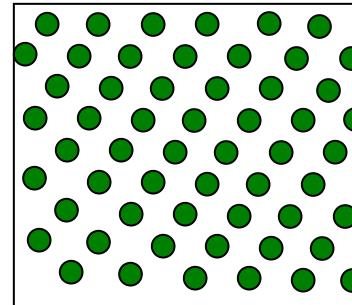


Interference between radiation scattered by distinct objects

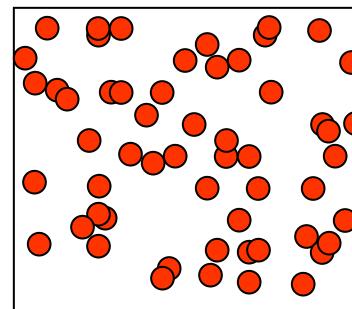
$$S(Q) = 1 + \frac{4\pi N_p}{QV} \int_0^\infty [g(r) - 1] r \sin(Qr) dr$$

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

Radial distribution function,
provides information about their
relative position

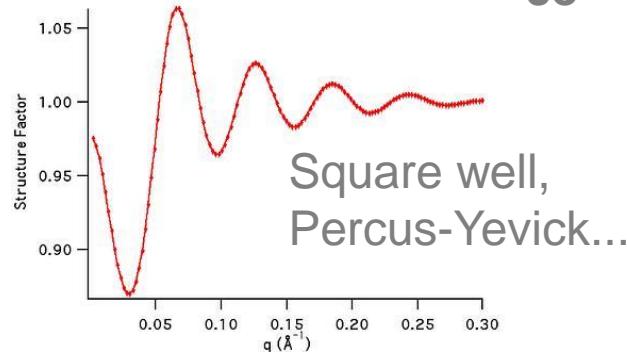
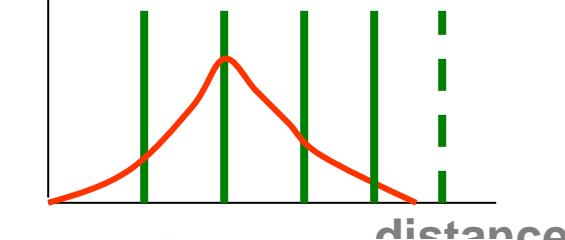


Ordered structure
'crystal'



Disordered structure

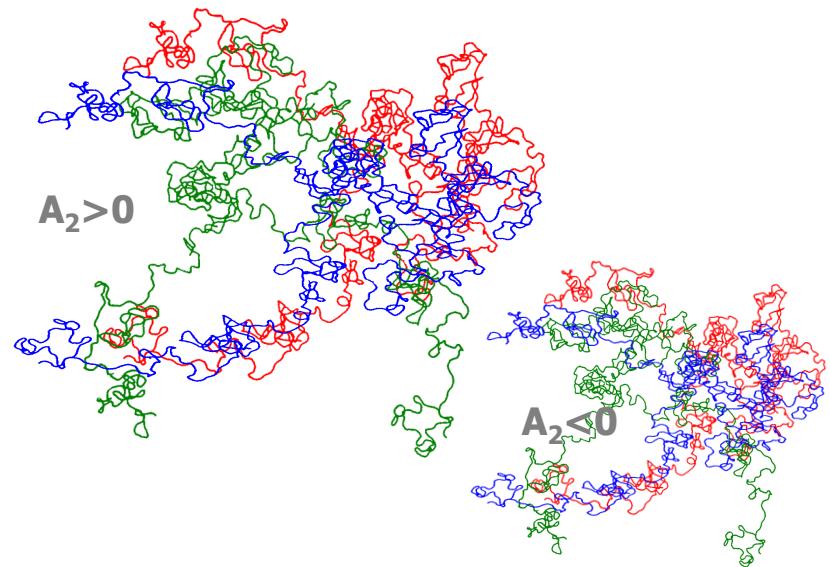
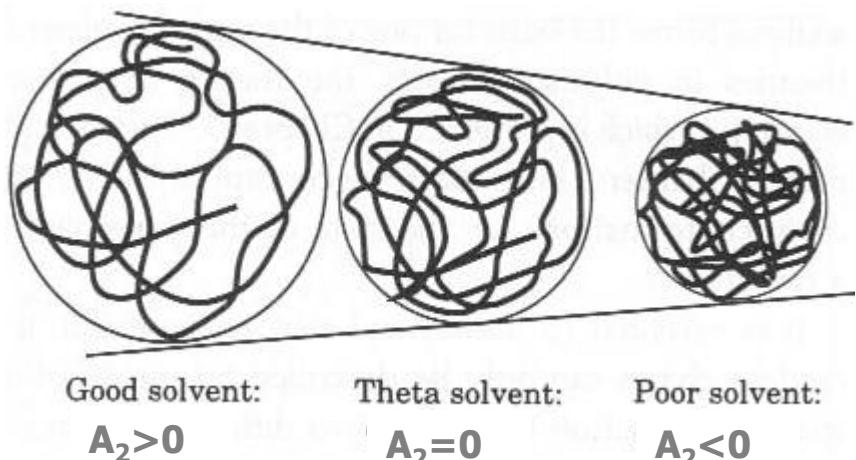
histogram



Square well,
Percus-Yevick...

Interactions: Polymers in solution and melt

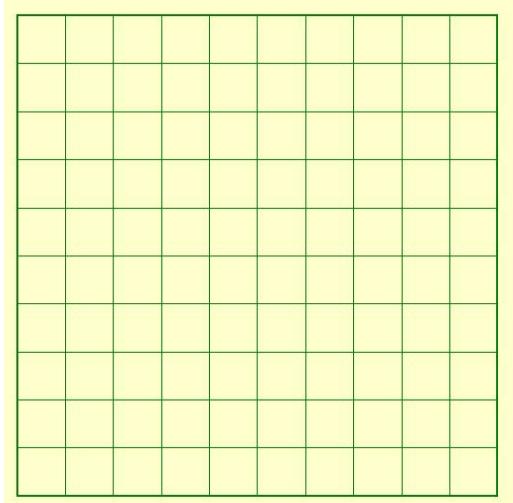
1953 Flory described the shape and size of individual polymer molecules in solutions and melts.



Ideal chains occur in θ -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 χ (for polymer mixtures)

Polymer miscibility (1)

**Flory-Huggins
lattice**



Binary mixture

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

Combinatorial entropy

$$-\frac{\Delta S}{R} = n_A \ln \phi_A + n_B \ln \phi_B \quad \Omega \text{ Boltzmann law}$$

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

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

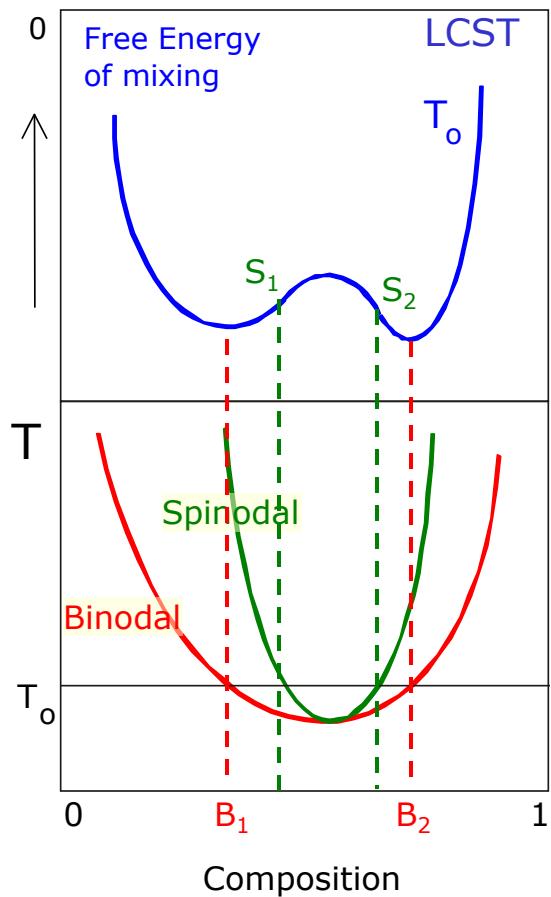
Combinatorial
entropy

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

$$\left\{ \begin{array}{l} \frac{\partial \Delta G_m}{\partial \phi_{B1}} = \frac{\partial \Delta G_m}{\partial \phi_{B2}} \equiv \mu \\ \Delta G_m(\phi_{B1}) + \Delta G_m(\phi_{B2}) = \min \end{array} \right.$$

'minima'

Spinodal

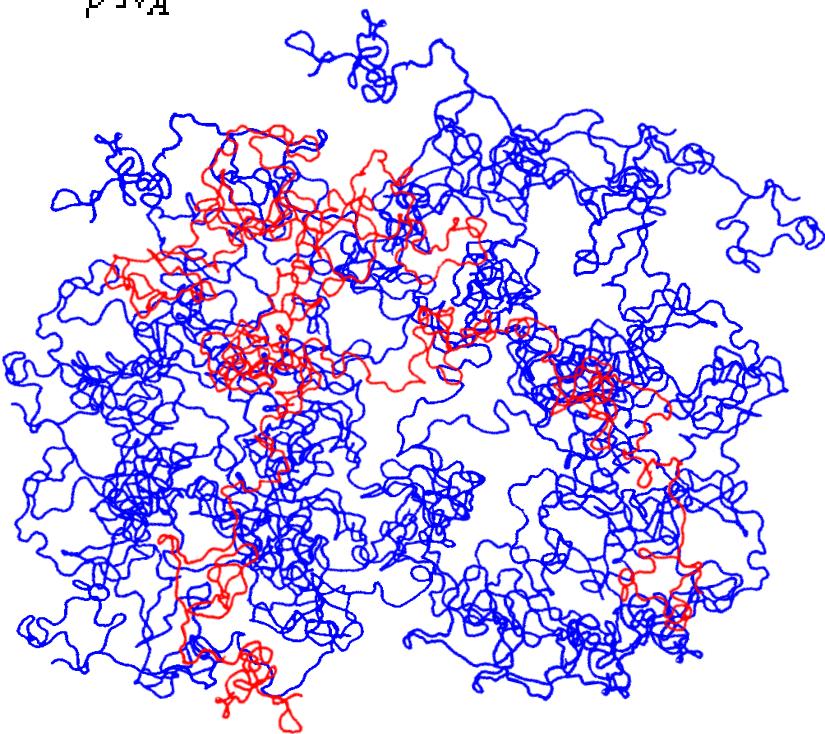
$$\frac{\partial^2 \Delta G_m}{\partial \phi^2} = 0$$

inflection points

Isotopic polymer mixture

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

$$\begin{aligned} \frac{1}{V} \left. \frac{d\sigma}{d\Omega}(q) \right|_{\text{eqm}} &= (b_D - b_H)^2 \phi(1 - \phi) \langle M' \rangle_w \frac{\rho N_A}{m^2} P(q) \\ &= (b_D - b_H)^2 \phi(1 - \phi) \langle M' \rangle_w \frac{(\Delta \phi)^2}{\rho N_A} P(q) \end{aligned}$$



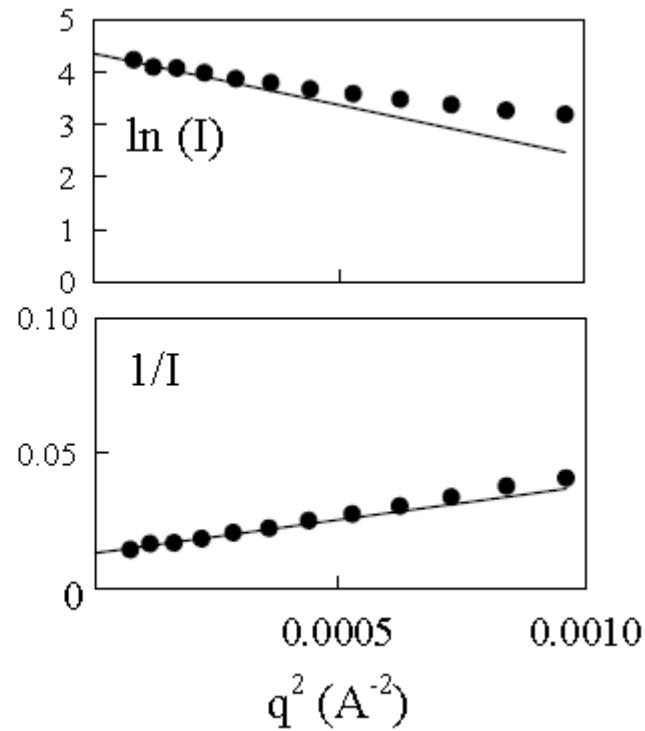
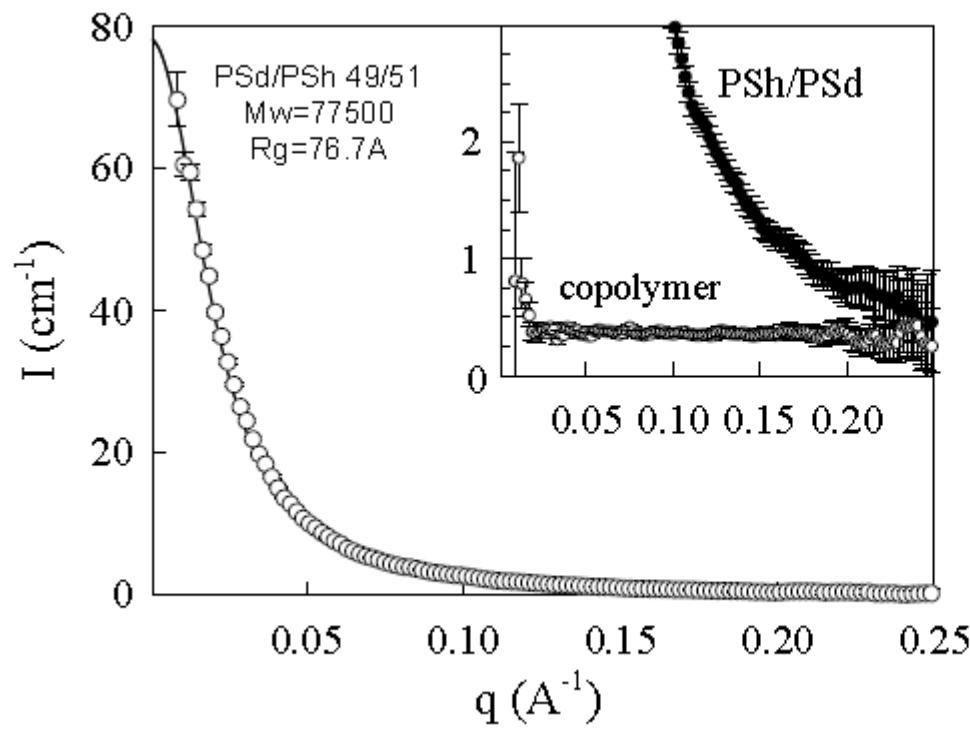
Approximations: Guinier & Zimm

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

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

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

for a polymer coil



Interacting polymer mixtures

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

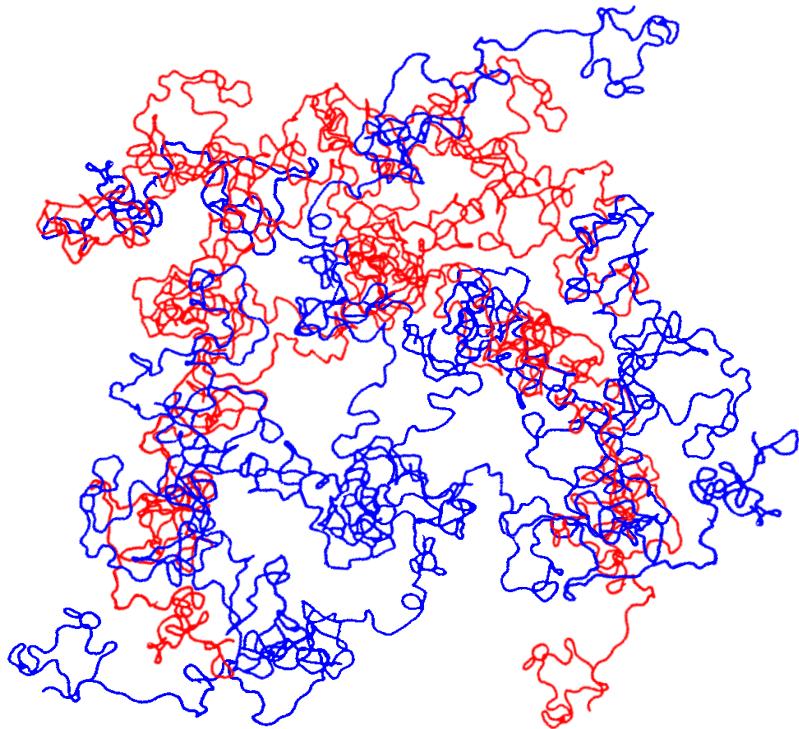
$$\frac{1}{S(q)} = \frac{1}{S_1(q)} + \frac{1}{S_2(q)} - 2 \frac{\tilde{\chi}_{12}}{v_0}$$

$$S(q) = \phi_1 v_1 \langle N_1 \rangle_\omega \langle g_D(R_{gq}^2 q^2) \rangle_\omega$$

Zimm $S(q) \approx \phi_1 v_1 \langle N_1 \rangle_\omega \left(1 - \frac{1}{3} \langle R_{gq}^2 \rangle_z q^2 \right)$

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

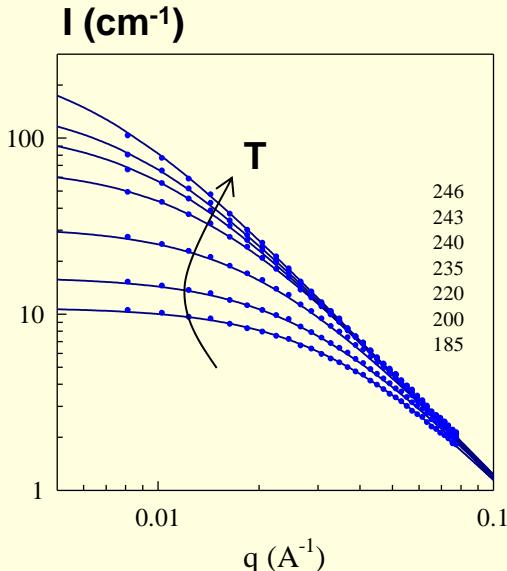
$$\frac{1}{S(0)} = \frac{1}{\phi_1 v_1 \langle N_1 \rangle_\omega} + \frac{1}{\phi_2 v_2 \langle N_2 \rangle_\omega} - 2 \frac{\tilde{\chi}_{12}}{v_0}$$



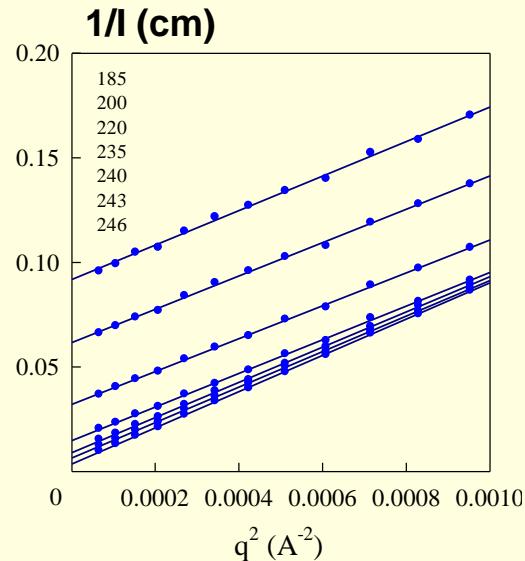
Equilibrium: SANS

TMPC/PSd 50/50

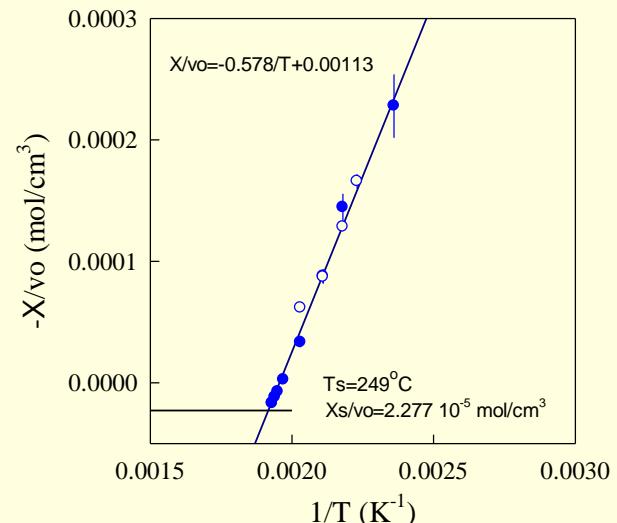
1-phase scattering



Orstein-Zernike



Interaction χ FH



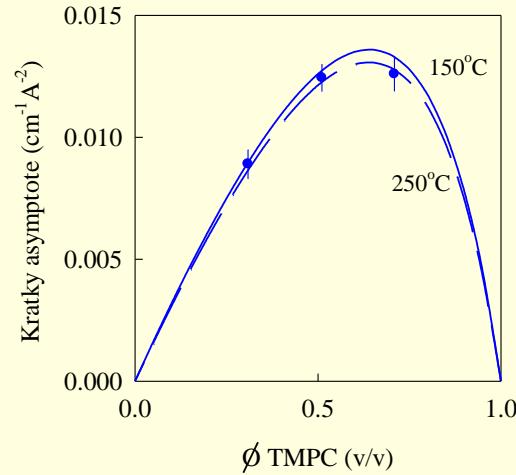
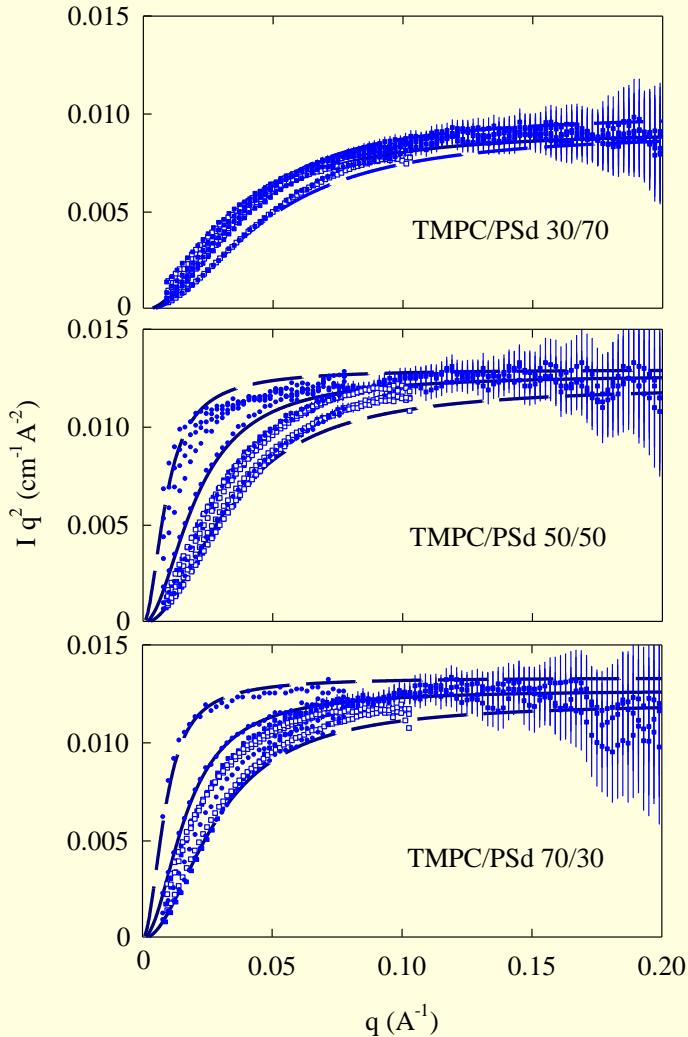
Random Phase Approximation

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

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

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

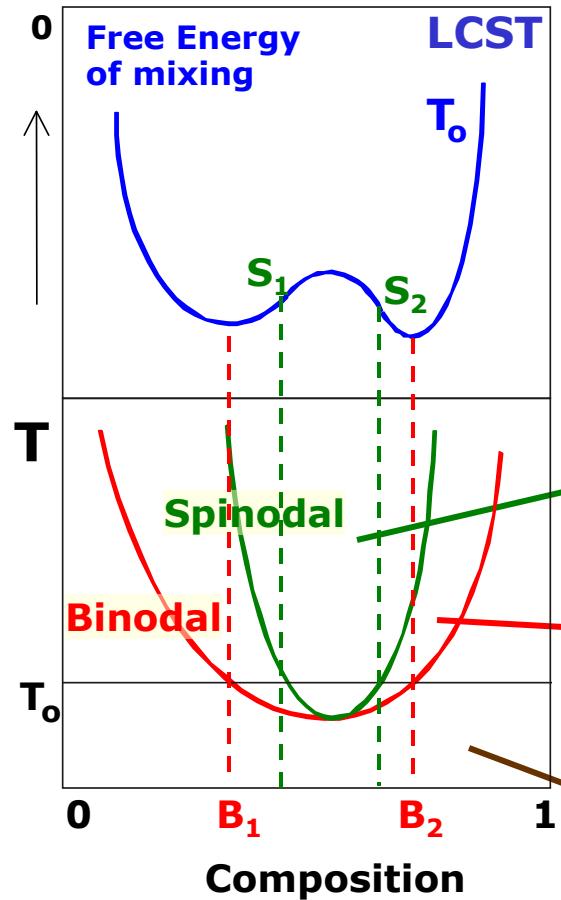
Equilibrium: Kratky asymptote



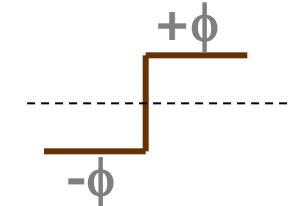
Kratky asymptote and segment length

$$S(q) \approx \frac{12\phi_1\phi_2}{q^2} \frac{v_o}{\hat{a}^2} \quad \frac{\hat{a}^2}{v_0} \equiv \phi_1\phi_2 \left(\frac{a_1^2}{\phi_1 v_1} + \frac{a_2^2}{\phi_2 v_2} \right)$$

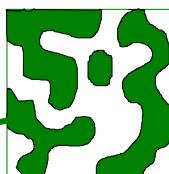
Non-equilibrium: Fluctuations & Phase separation



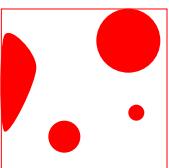
Concentration fluctuations



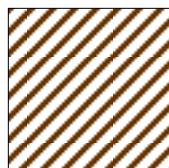
Unstable: $G'' < 0$
spinodal decomposition



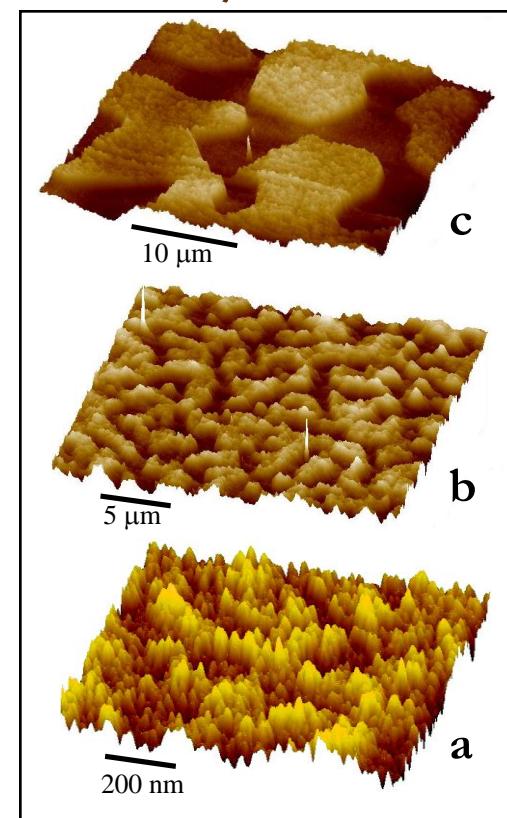
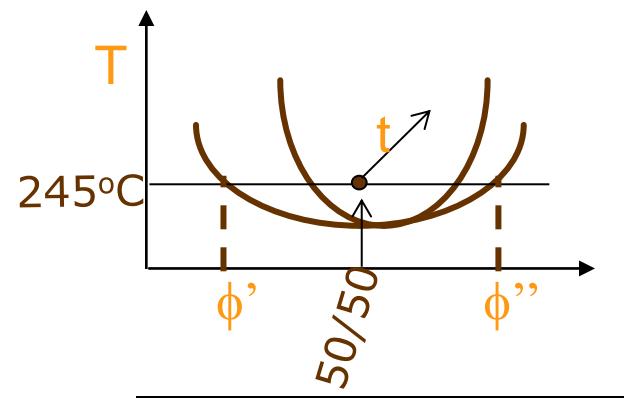
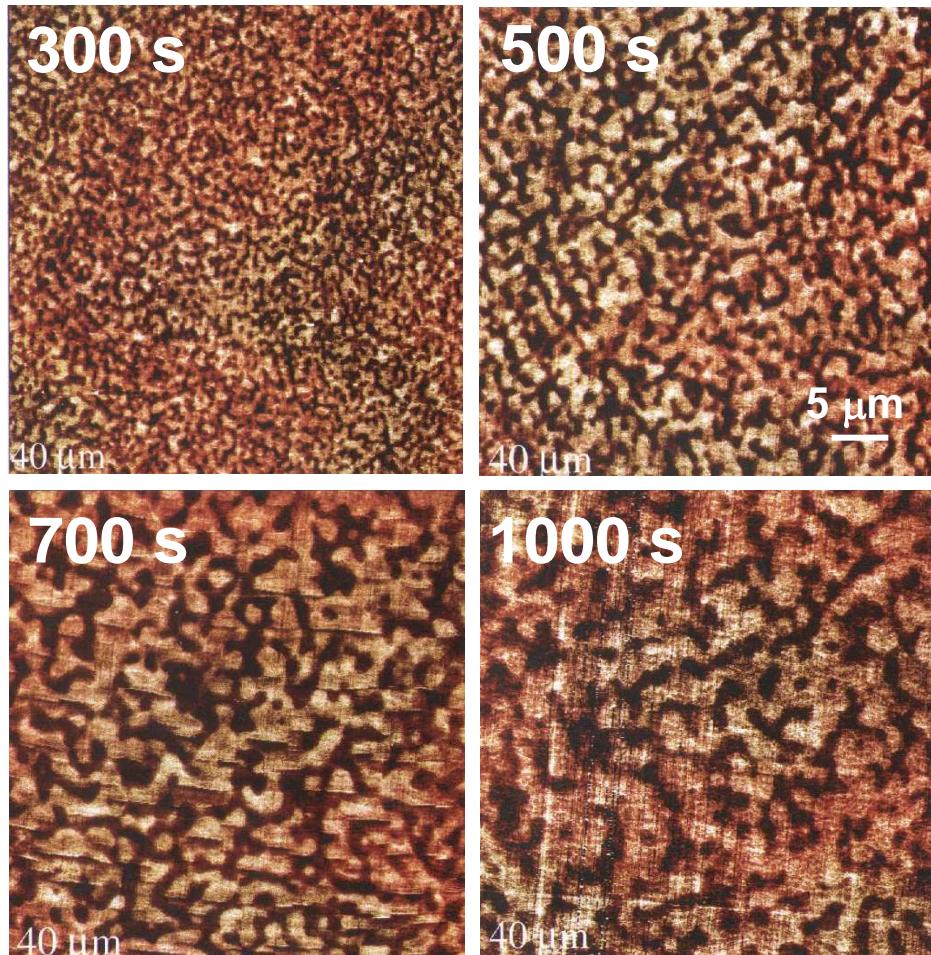
Metastable:
nucleation & growth



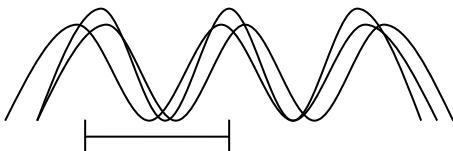
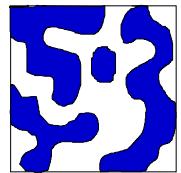
Stable:
equilibrium



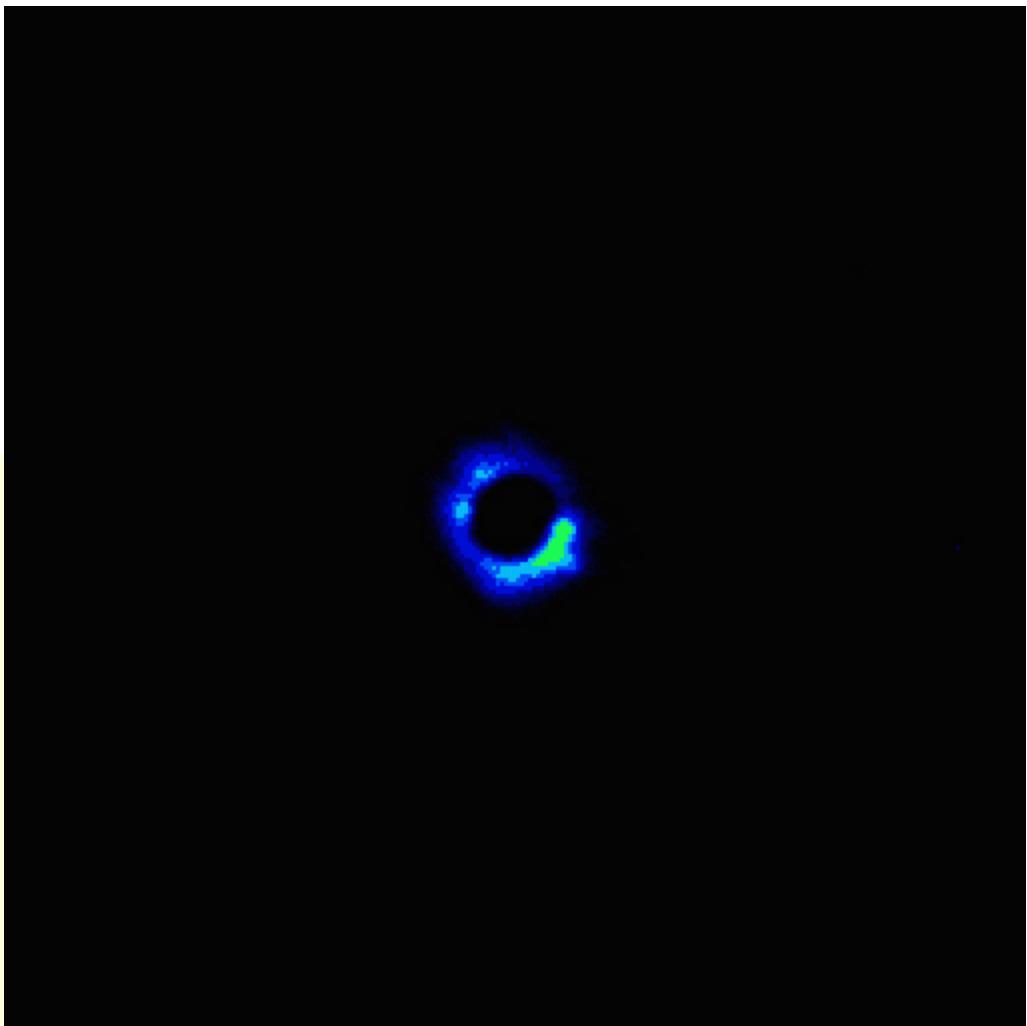
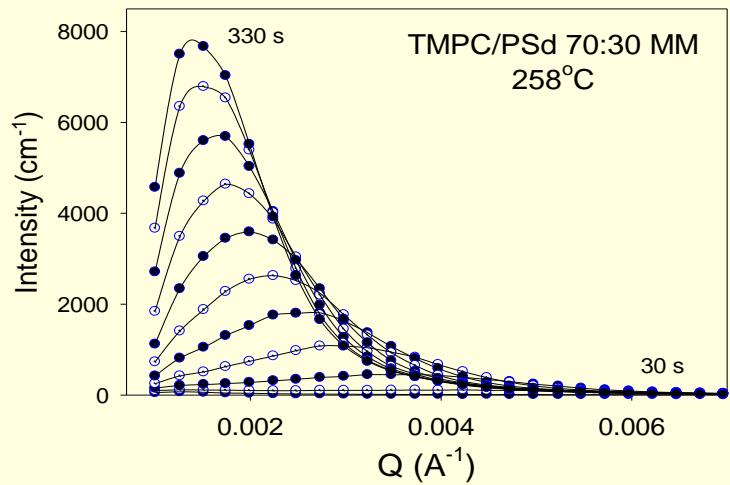
Phase separation: spinodal decomposition

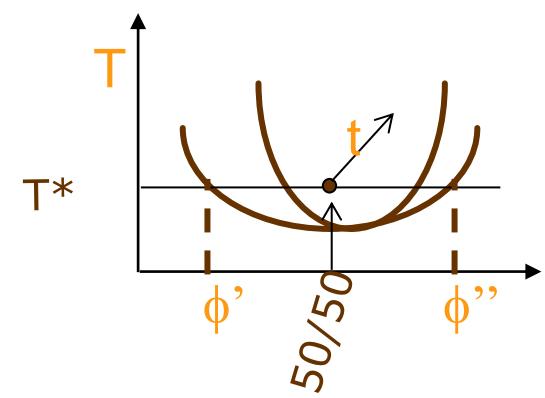
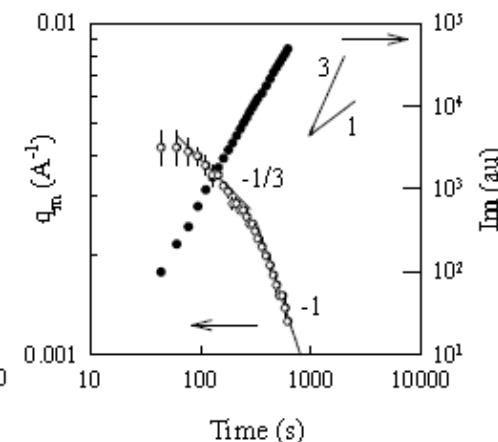
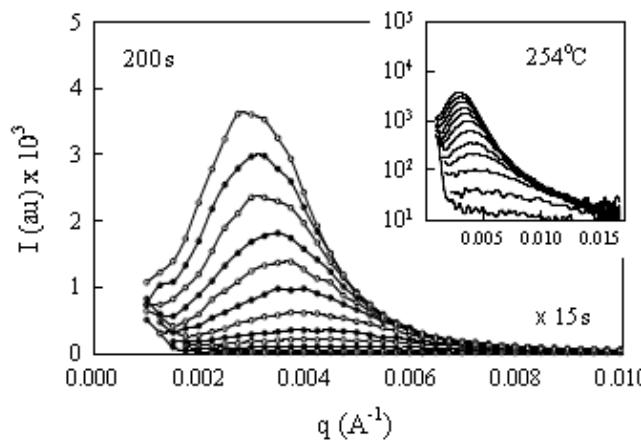
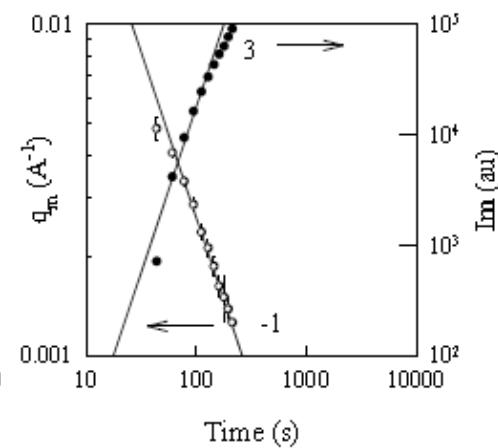
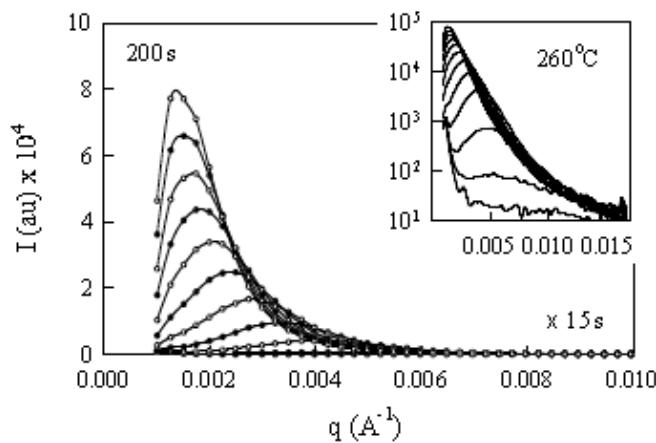
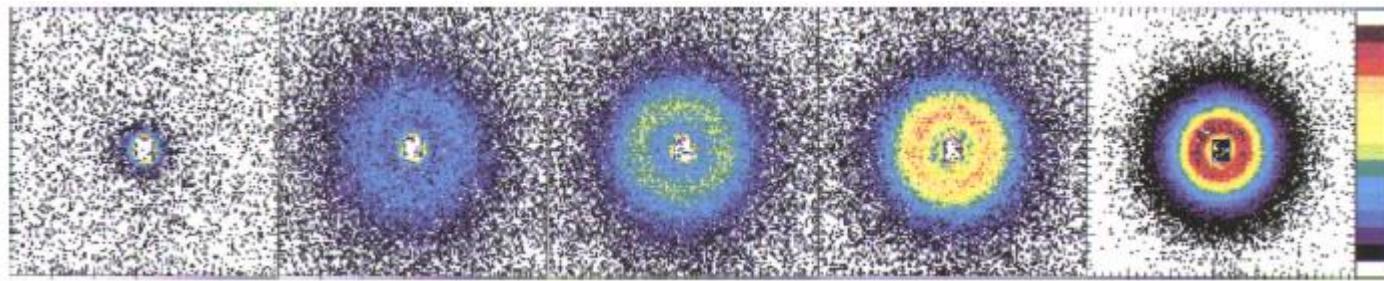


Phase separation



Λ_m : characteristic length of phase separation $\sim 10\text{s}-100\text{s nm}$

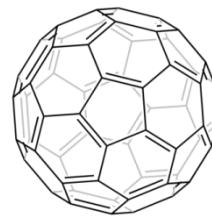
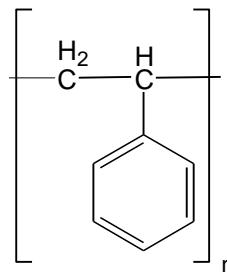
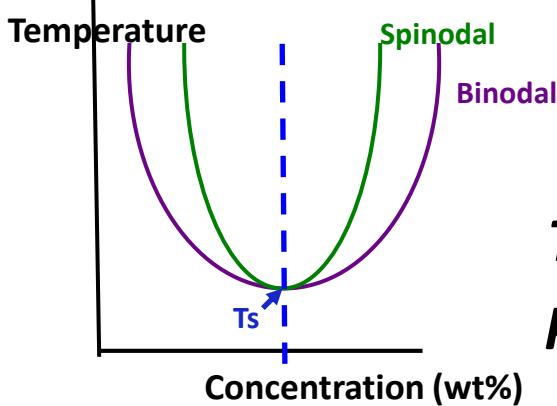




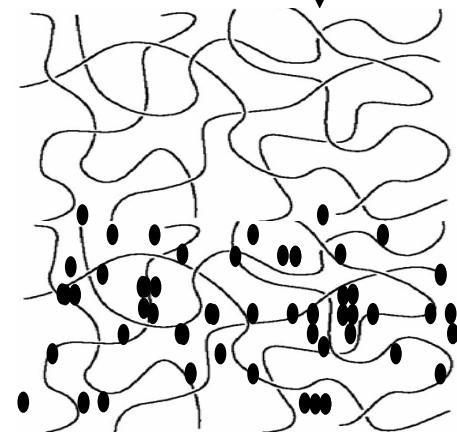
Opportunities & recent developments

nano*composites*

structure



dynamics

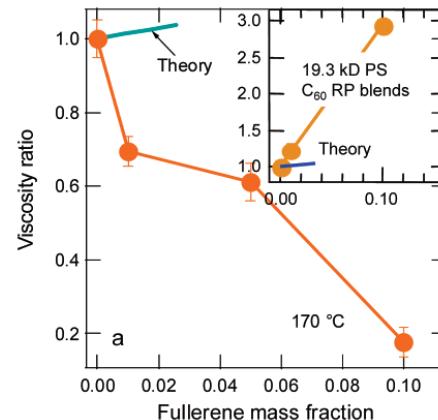
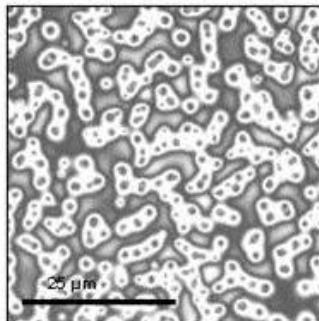


Bulk

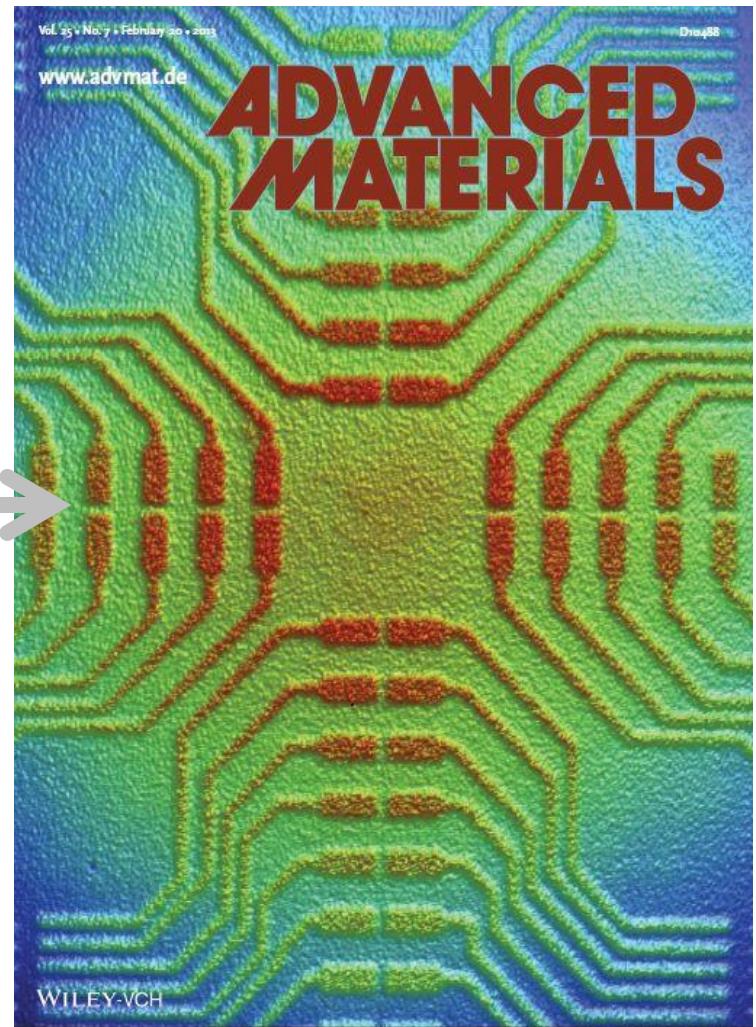
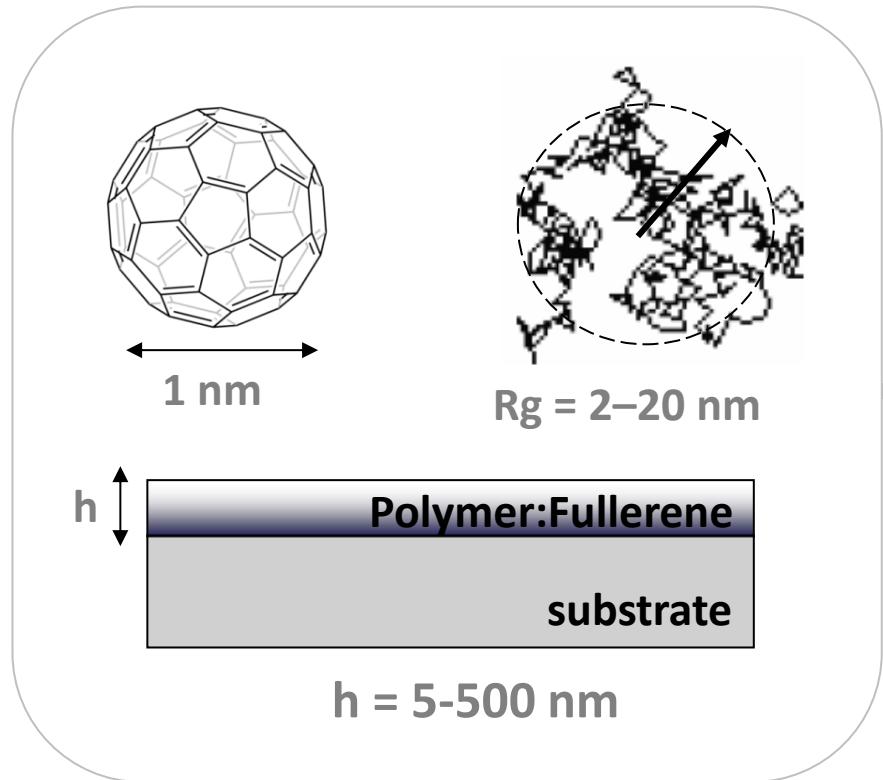
*Thermodynamics &
phase separation*

Thin Films

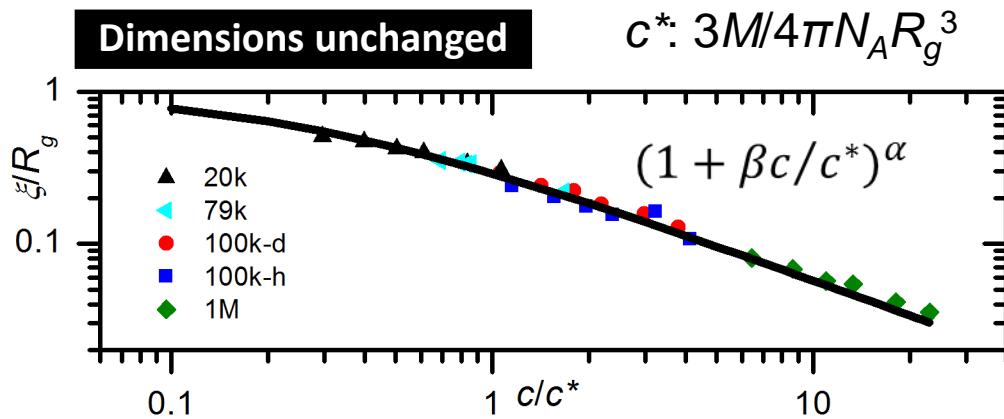
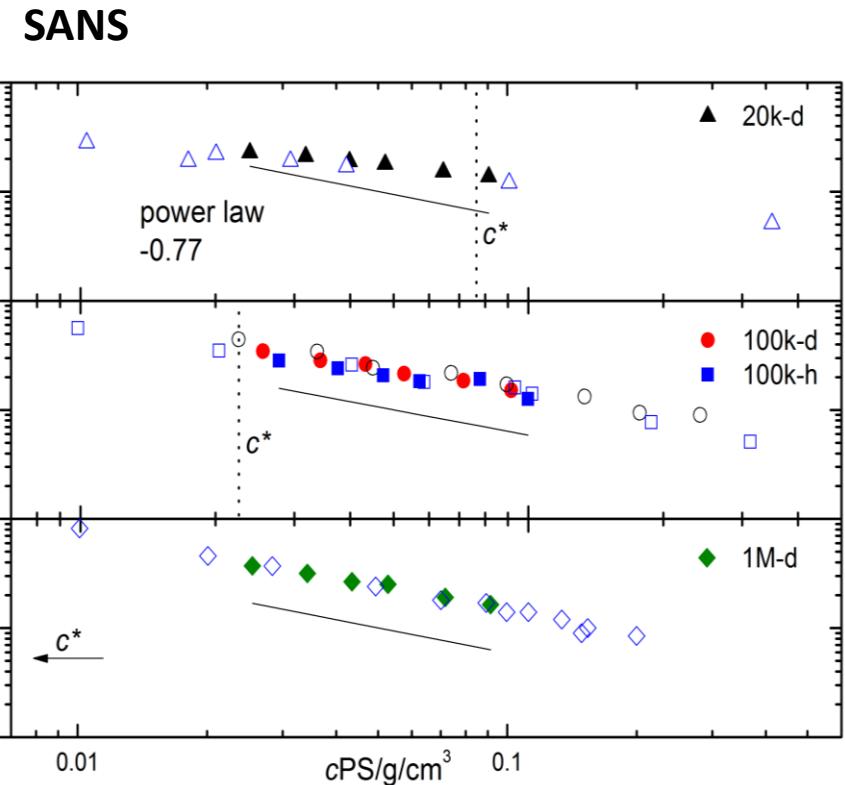
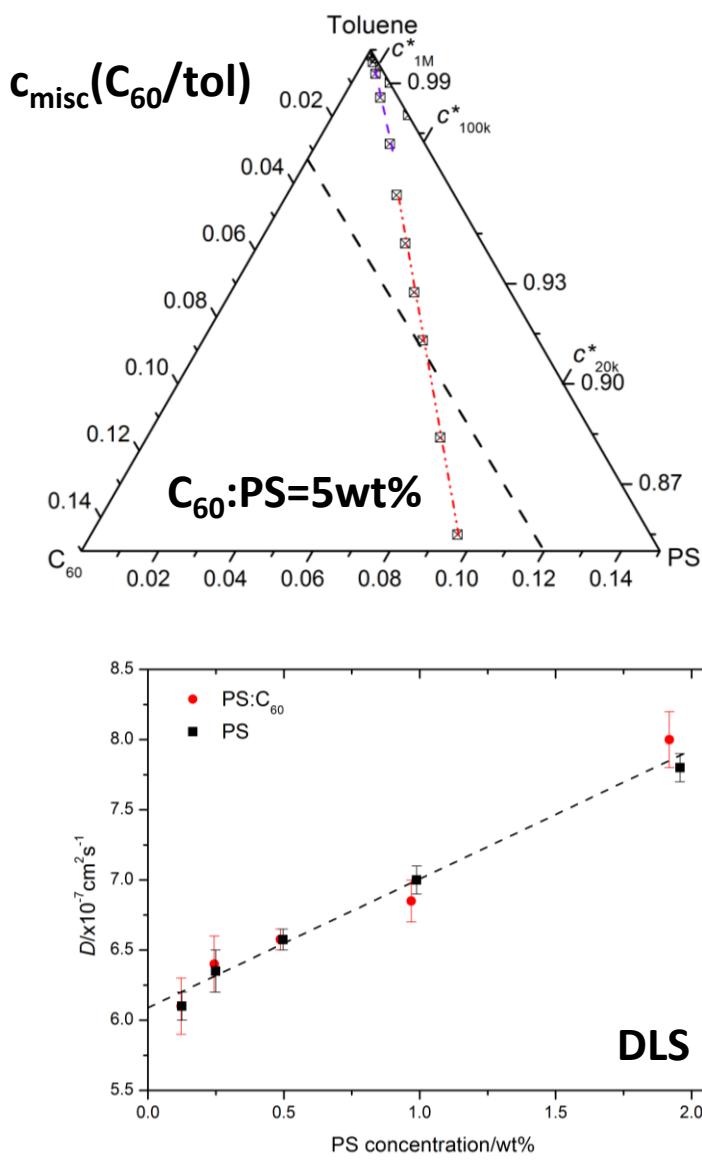
Morphology



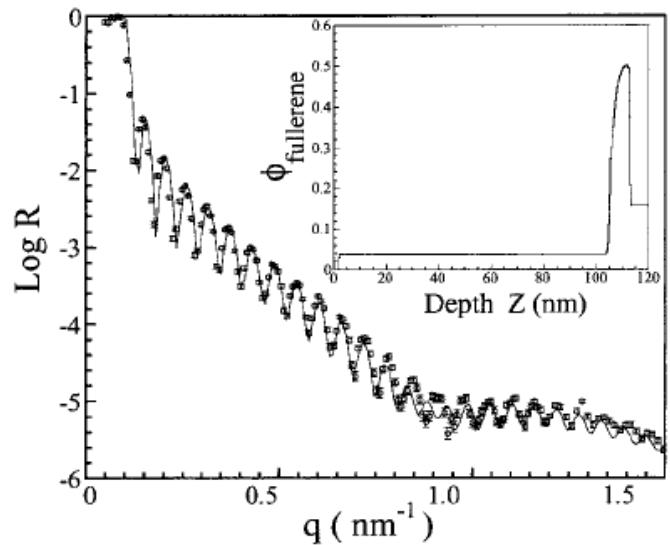
Polymer-fullerene blends



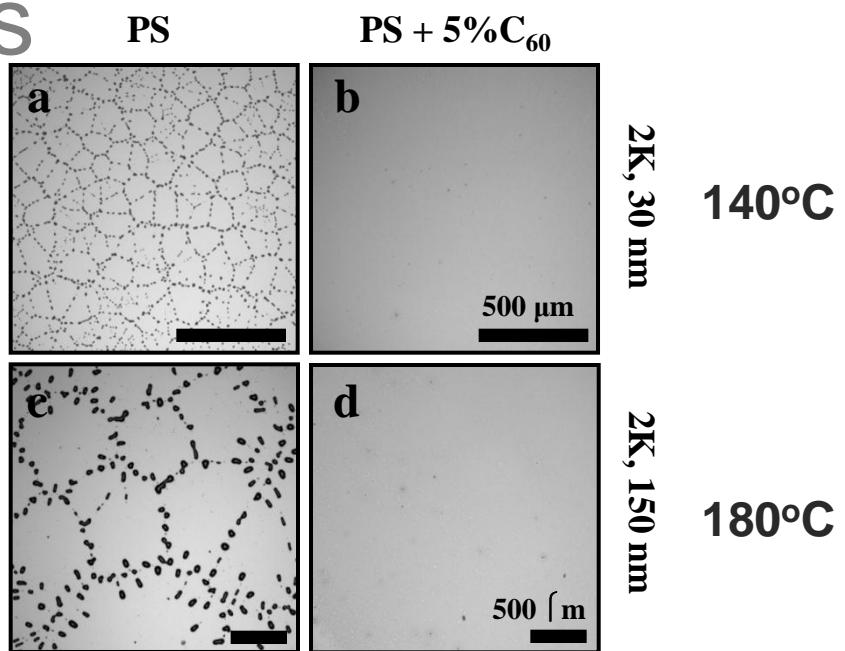
Polymer solution conformation + fullerenes



Design 3D composites

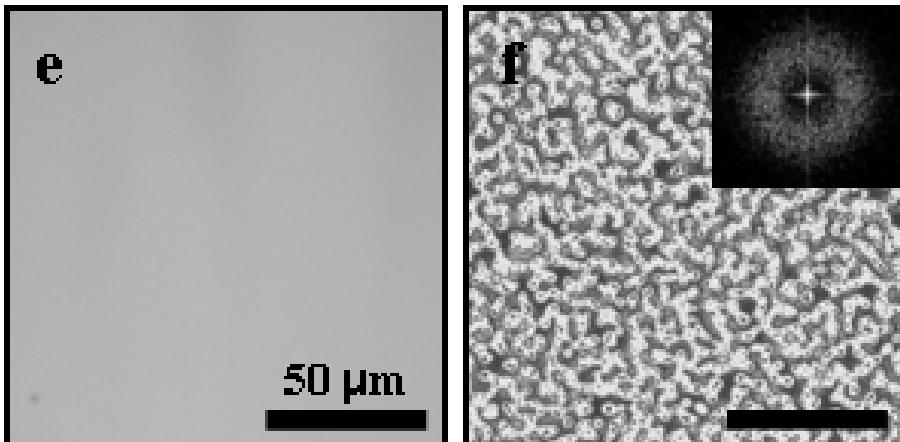


PS+5% C₆₀ h = 100nm



140°C

2K, 150 nm
180°C



270K, 150 nm
180°C

GISANS & reflectometry

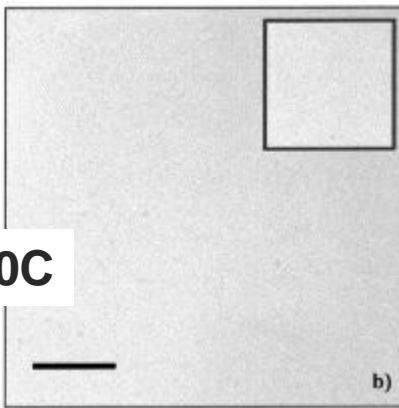
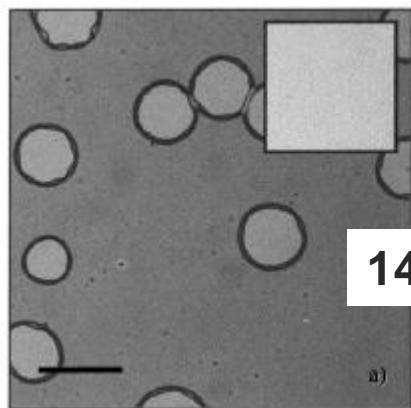
PRL 2010

‘Spinodal Clustering’

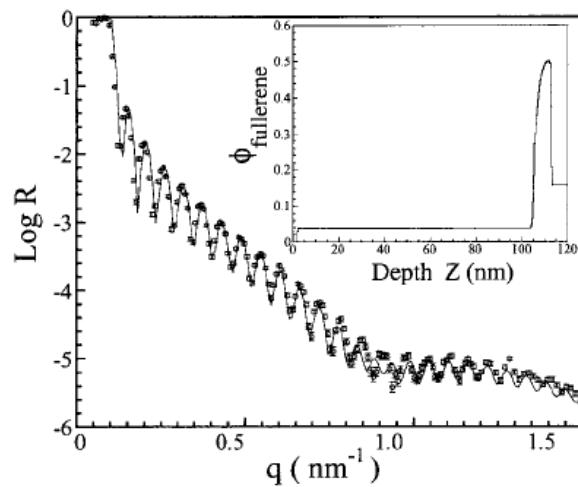
Thin films

PS (2k), 30 nm

1% C₆₀, 30 nm



140C

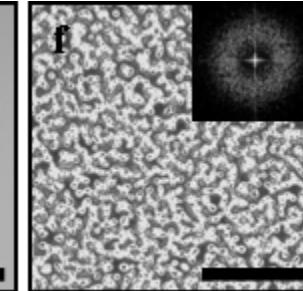
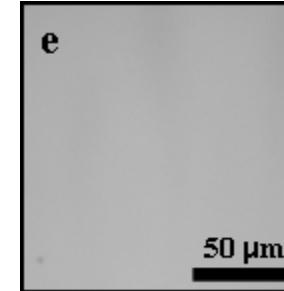
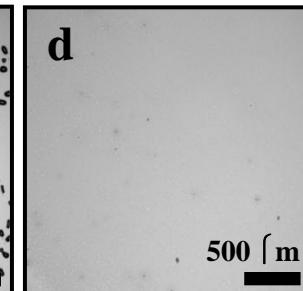
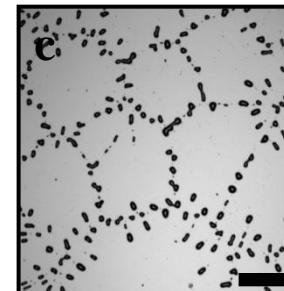
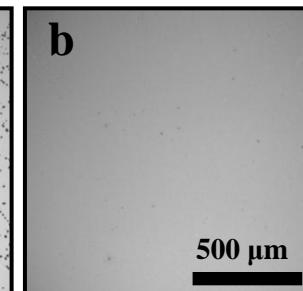
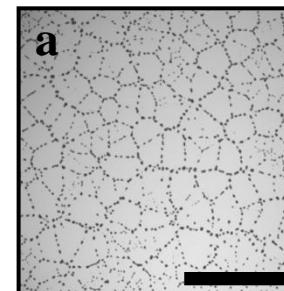


PS+5% C₆₀ h = 100nm

GISANS & reflectometry

PS

PS + 5% C₆₀



140°C

180°C

2k, 30 nm

2k, 150 nm

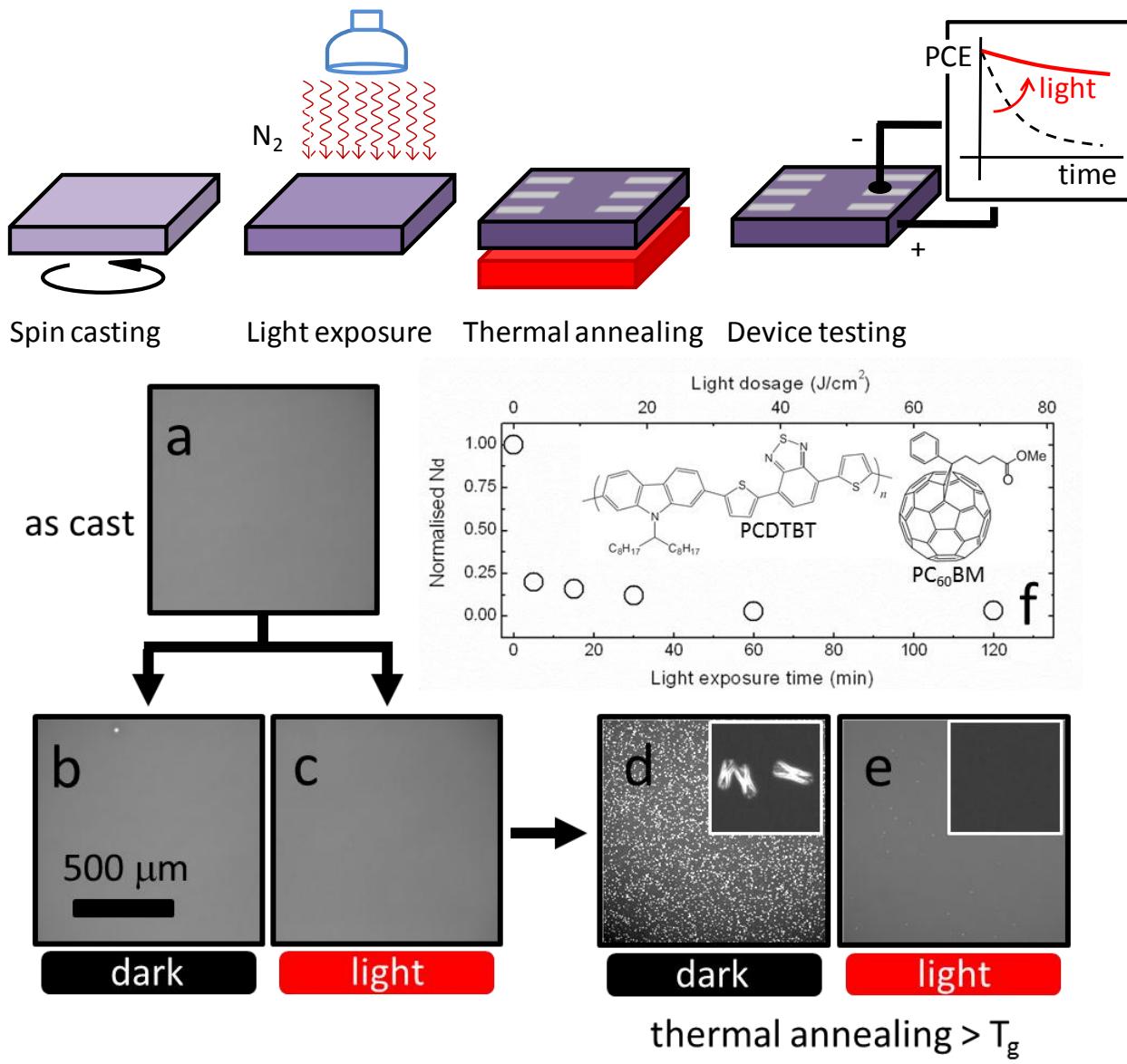
270K, 150 nm

180°C

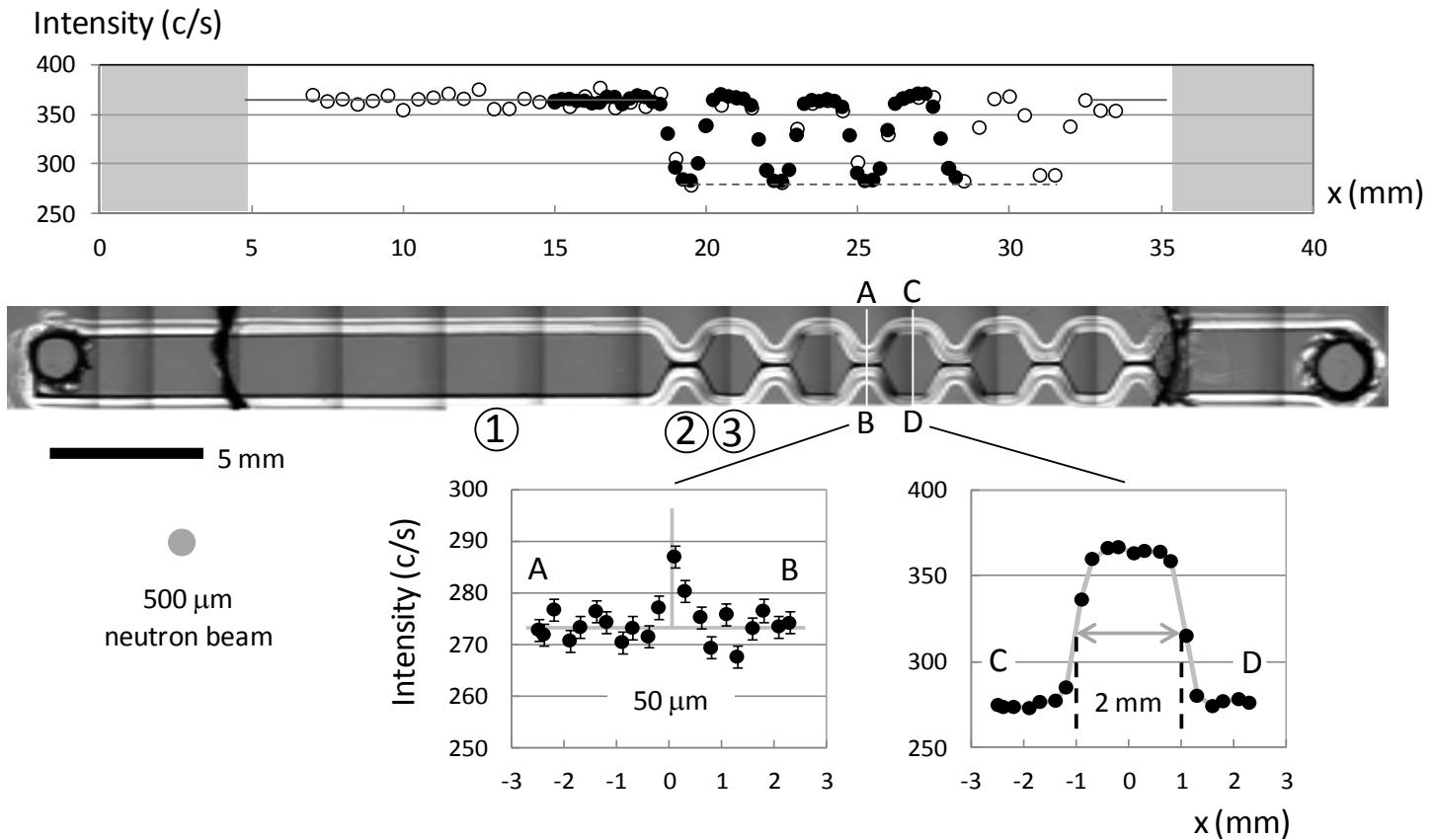
'Spinodal nucleation'

Phys. Rev. Lett. **105**, 038301 (2010)
Macromolecules **44**, 4530-4537 (2011)

Organic Solar Cell lifetime?

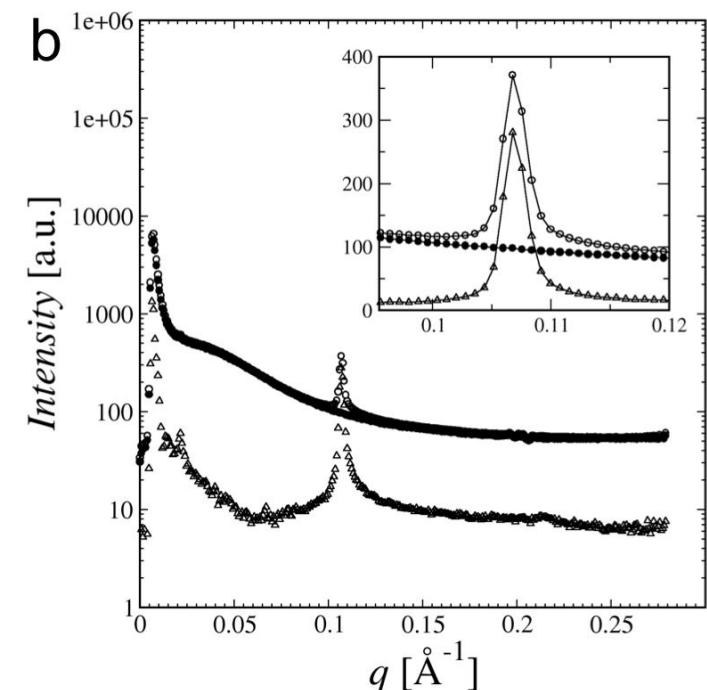
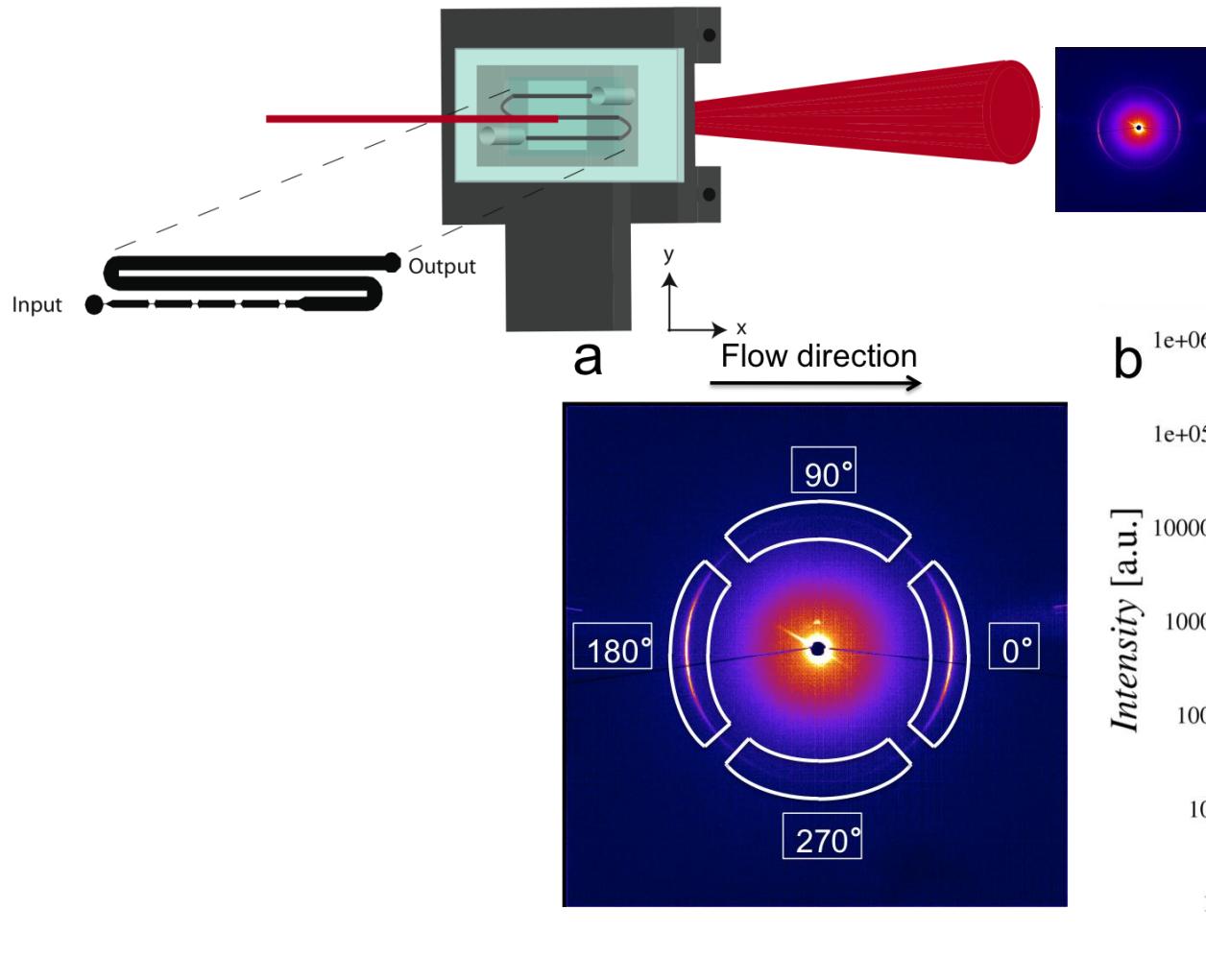


MicroSANS: microprocessing

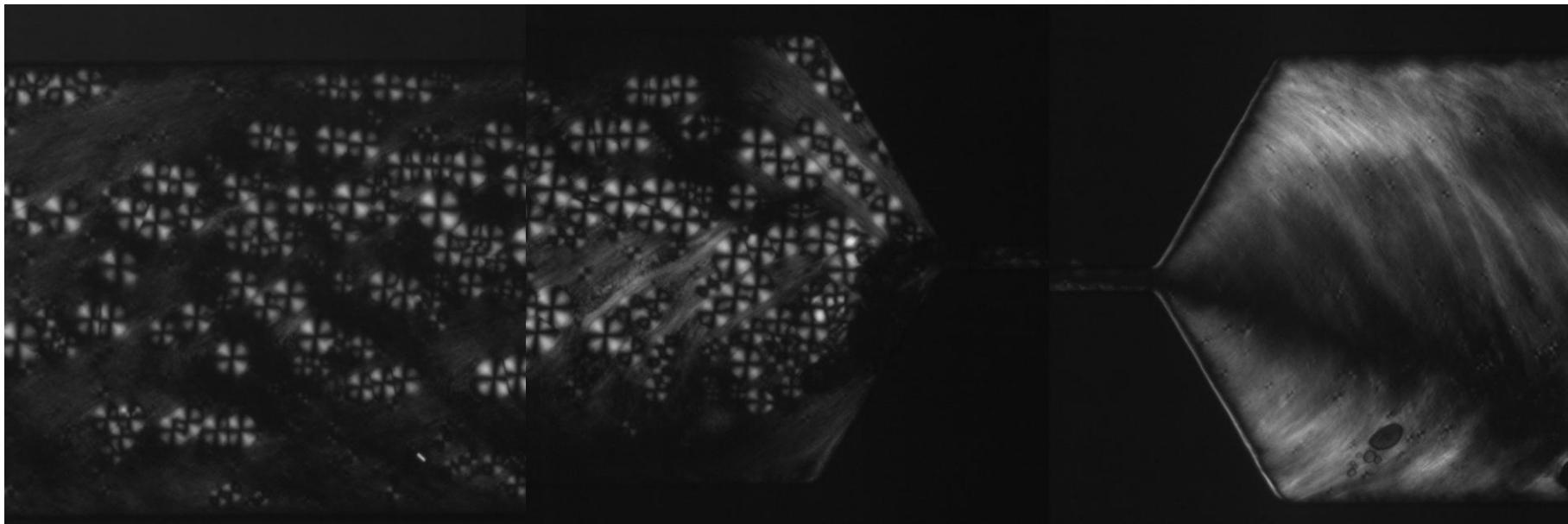


Flow fields (and microfluidics?)

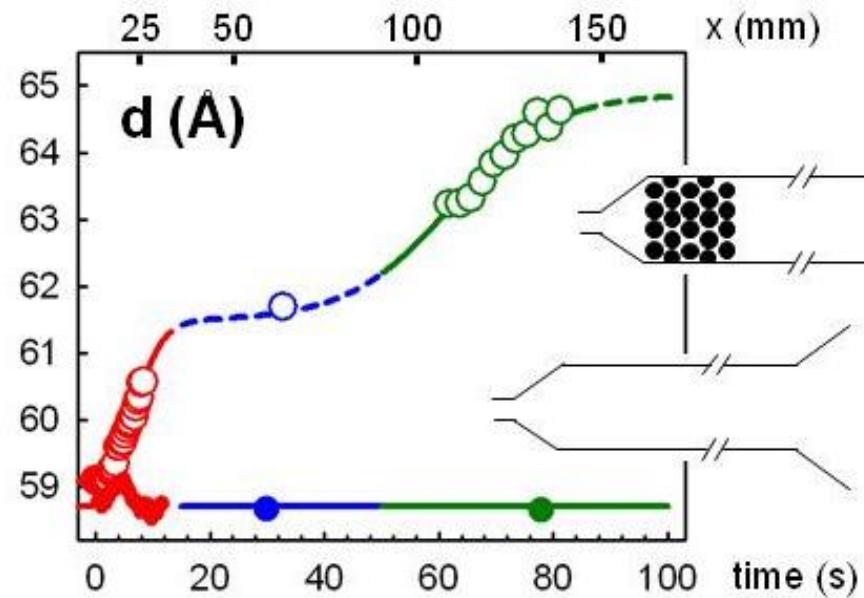
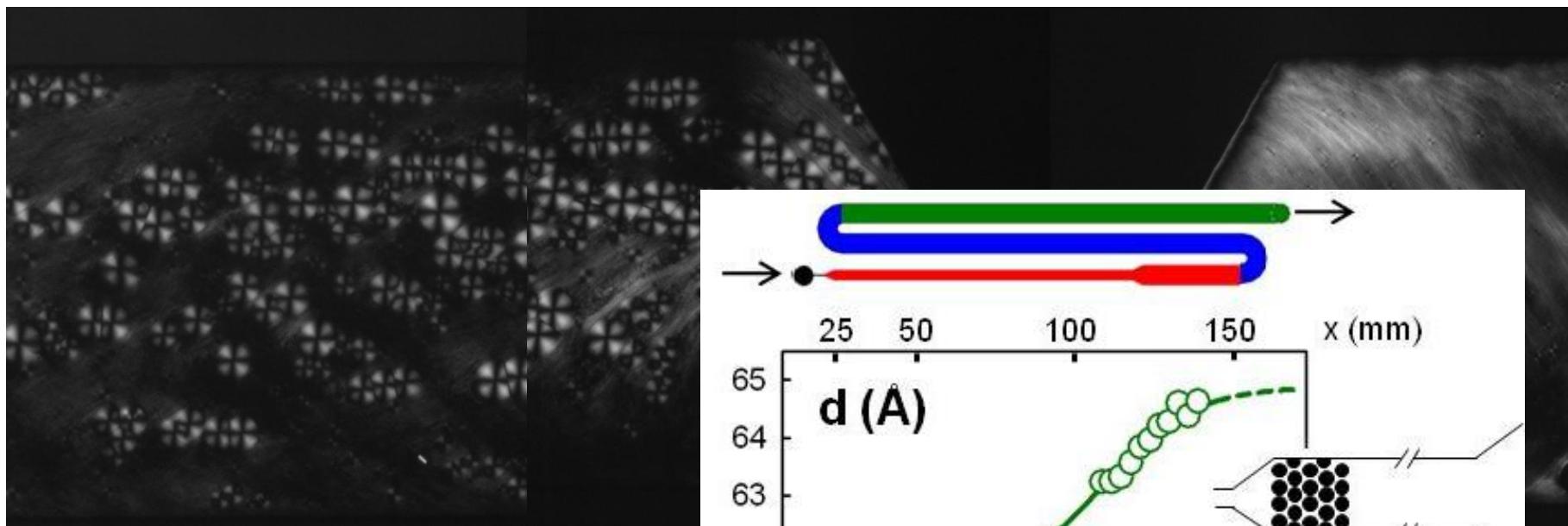
CTAC/ Pentanol/Water



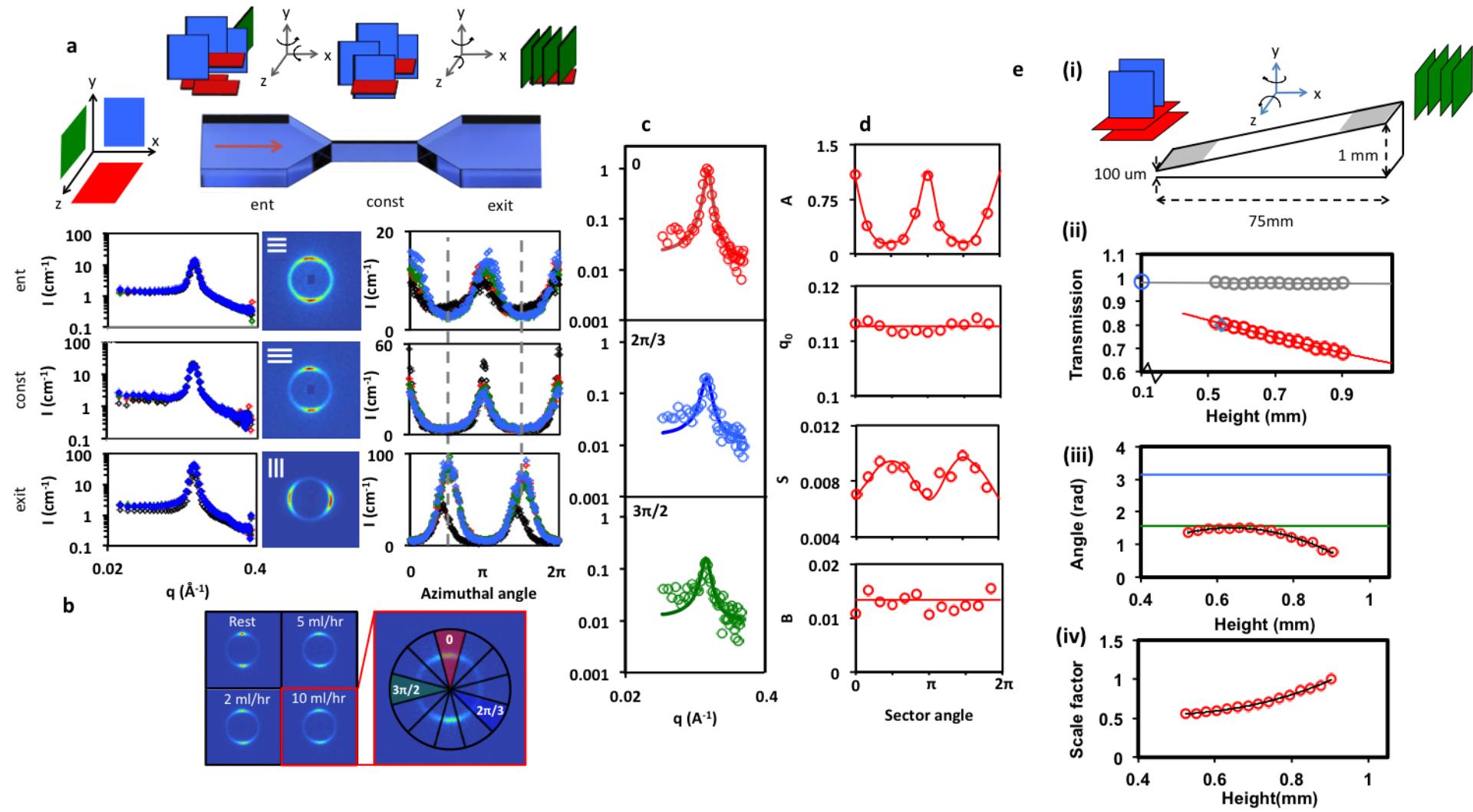
Microflow complex fluids



Microflow complex fluids

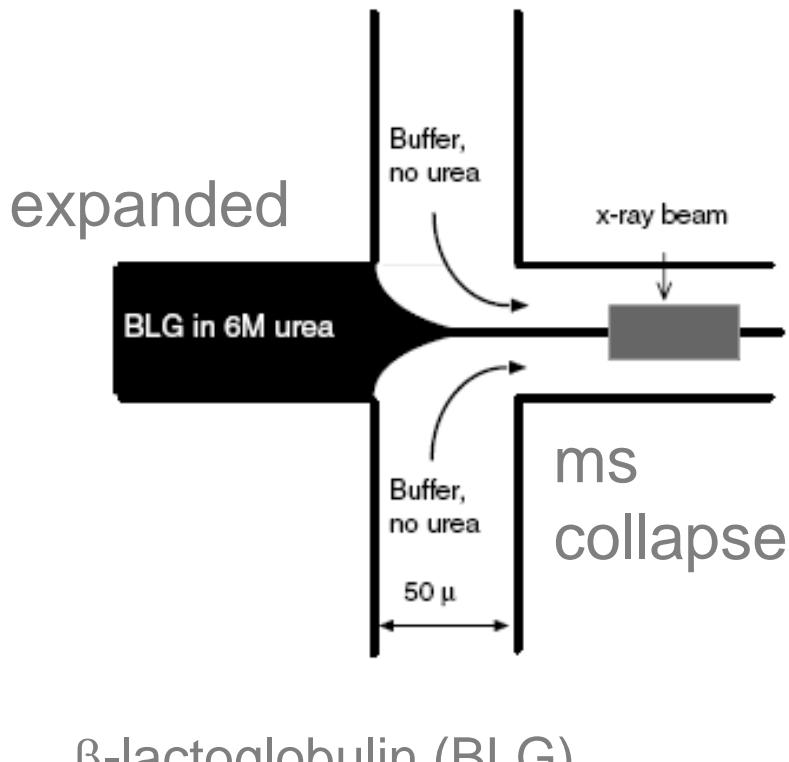


Mechanistic molecular insight SANS/XS

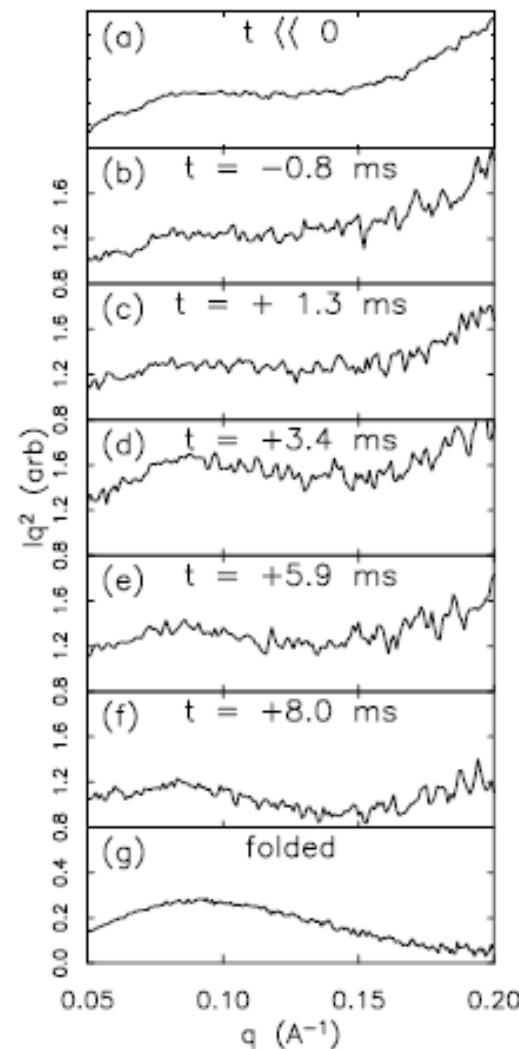


Spatio-temporal mapping:

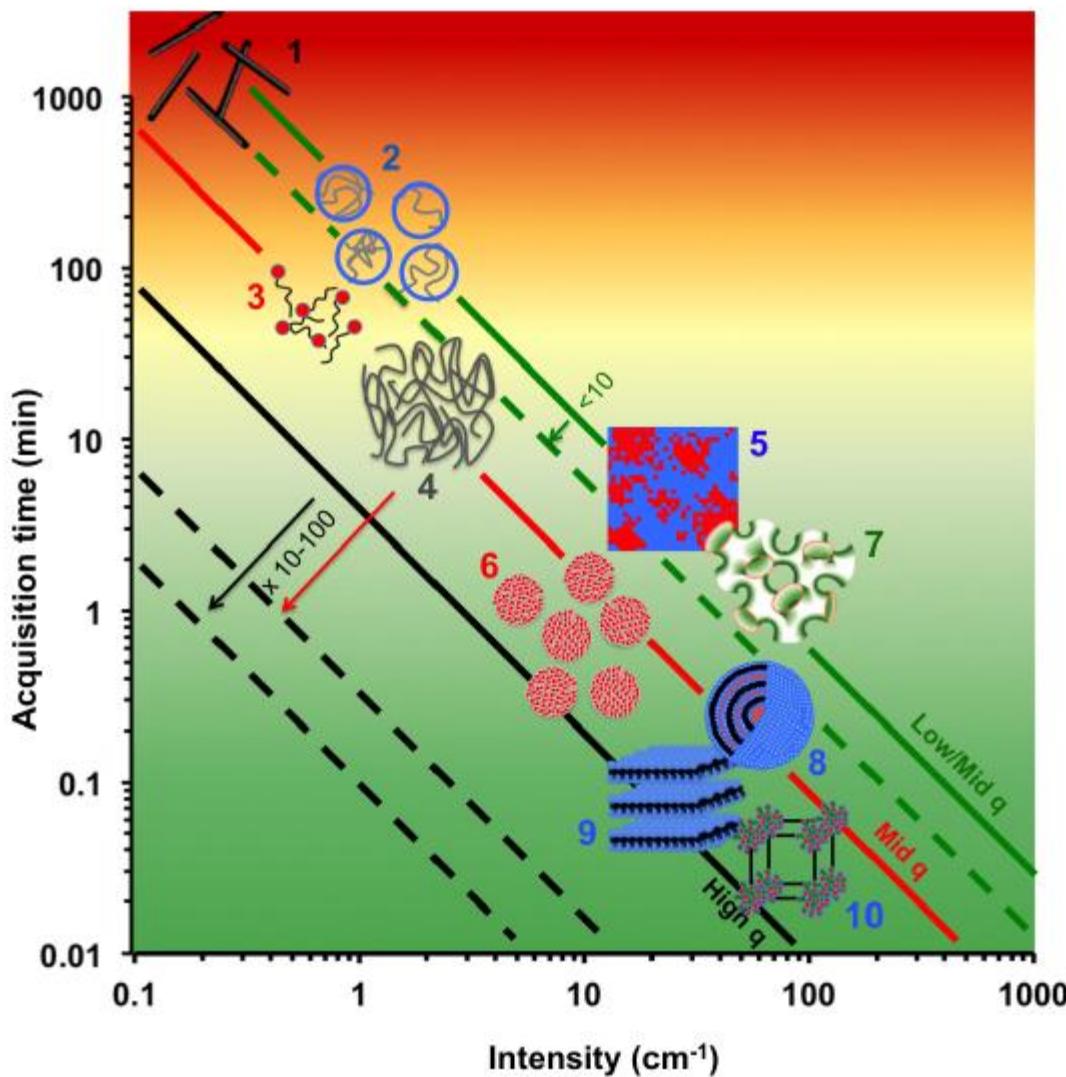
Coil-to-globule transition



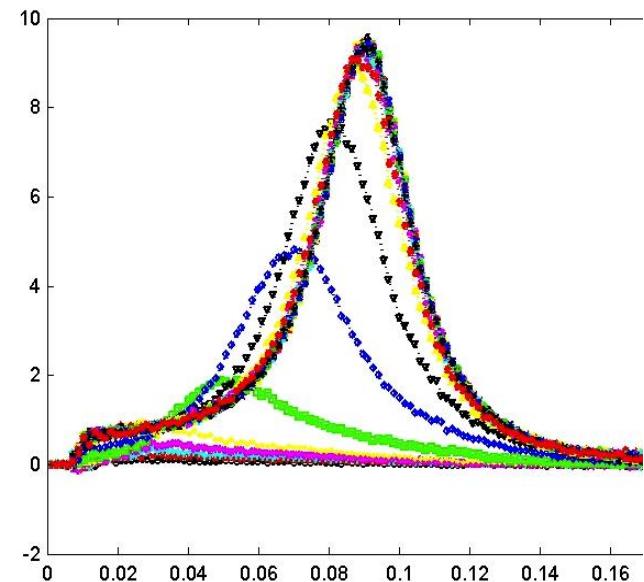
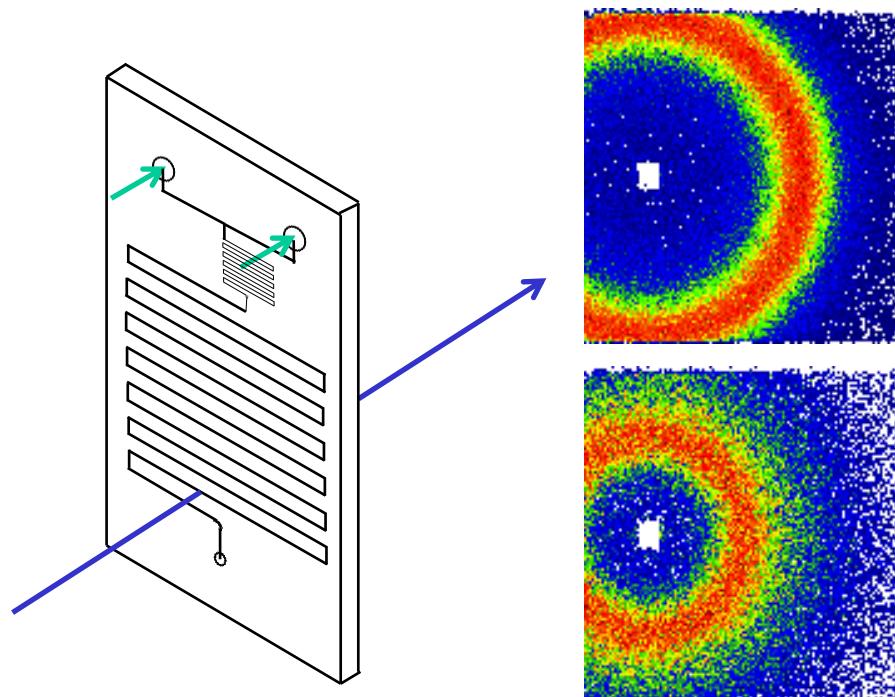
β -lactoglobulin (BLG)



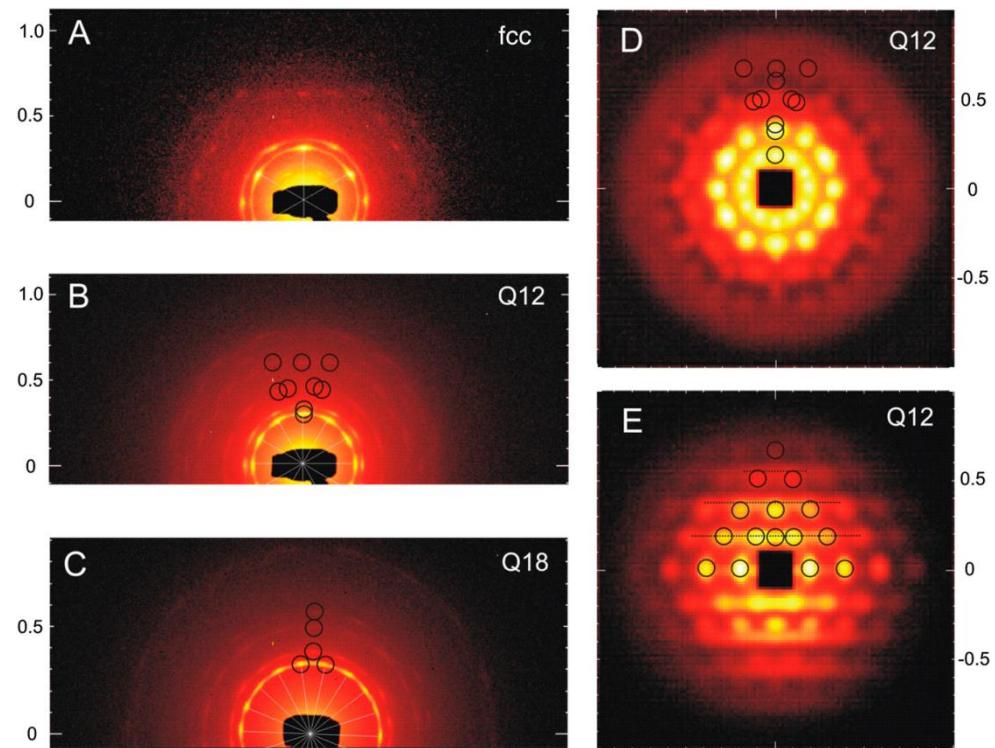
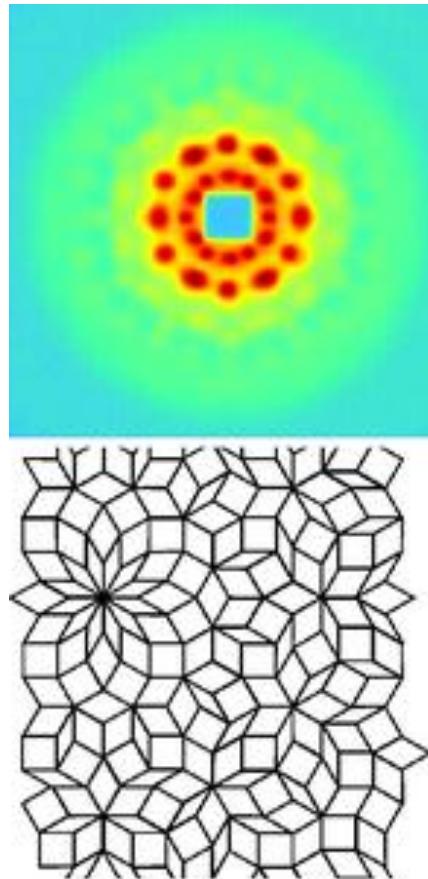
(Pollack, Austin, etc)



MicroSANS: High throughput



Soft colloids under flow



Forster et al. PNAS 2011

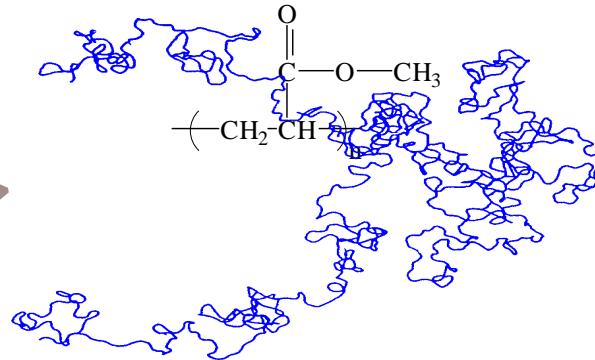
Summary

① Intro



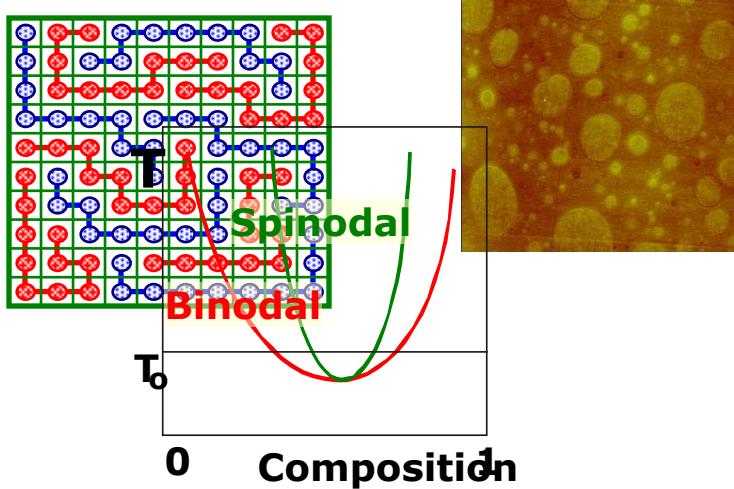
History

② Soft matter



③ Form and structure

④ Mixtures & design



⑤ Outlook

