Imperial College London

Neutrons in soft matter

Lecture 1 - Structure

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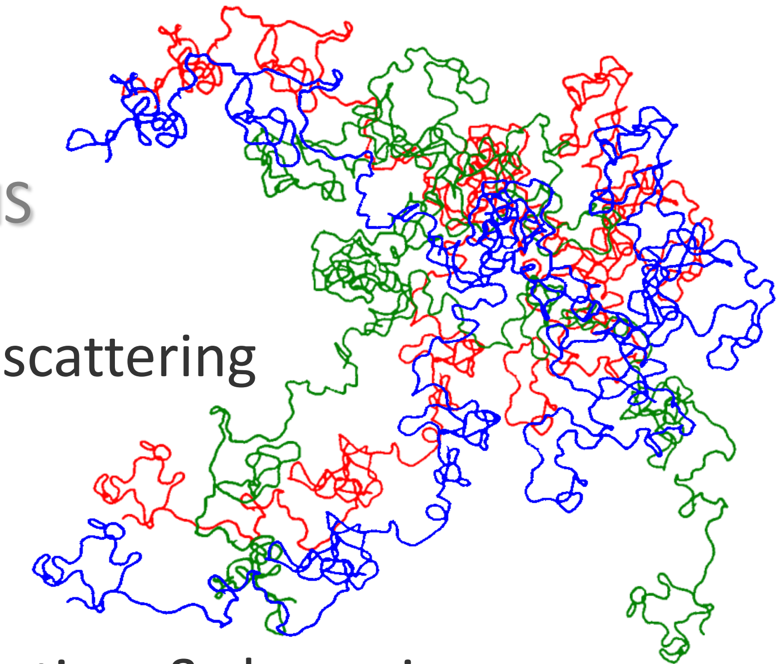
12th Oxford School on Neutron Scattering, 15-16 September 2011

Outline



Lecture 1 – Structure & kinetics – SANS

Introduction
  soft matter & relevance of neutron scattering

Single objects: spheres, coils, rods...

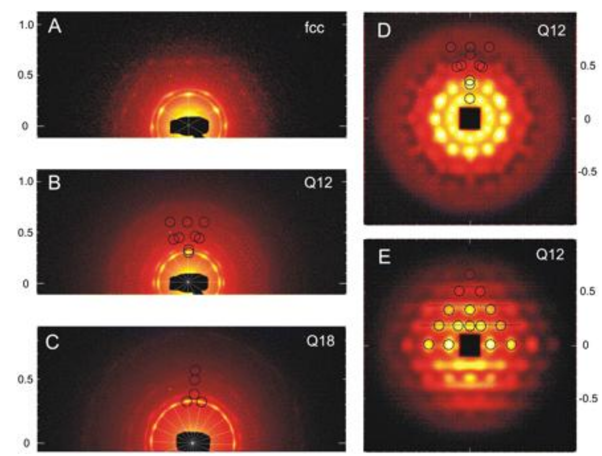
Single chain polymer conformation
  (solution and blends)

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

Lecture 2 – Interfaces and dynamics

Reflectivity and diffusion

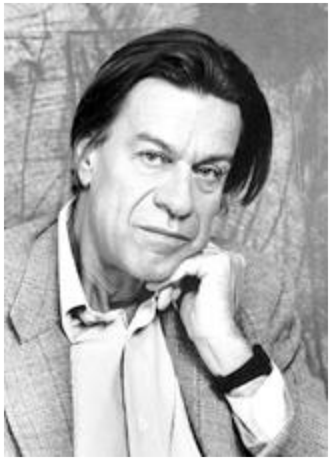
Dynamics in soft matter, QENS, BS, Spin-echo



Forster et al (2011)

Soft Matter

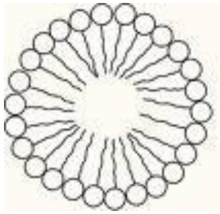
"molecular systems giving a strong response to very weak command signal"

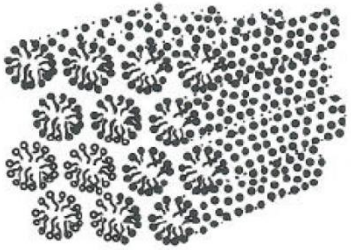


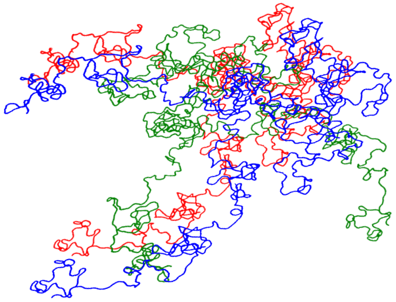
deGennes (1991)

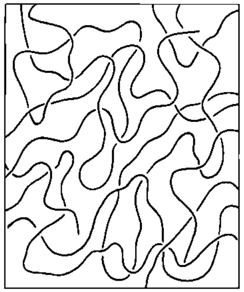
Condensed matter: states are easily deformed by small external fields, including thermal stresses and thermal fluctuations.

Relevant energy scale comparable with room temperature thermal energy.









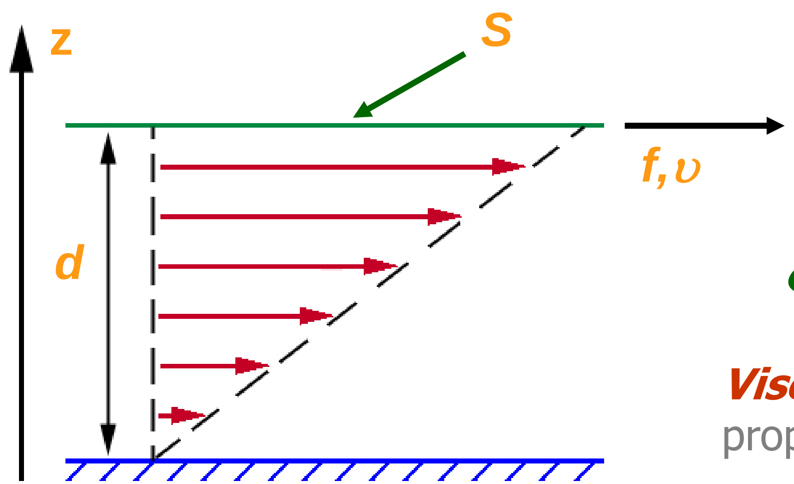
Complex fluids: including colloids, polymers, surfactants, foams, gels, liquid crystals, granular and biological materials.

shear

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

Viscosity

Simplest setup to measure viscosity

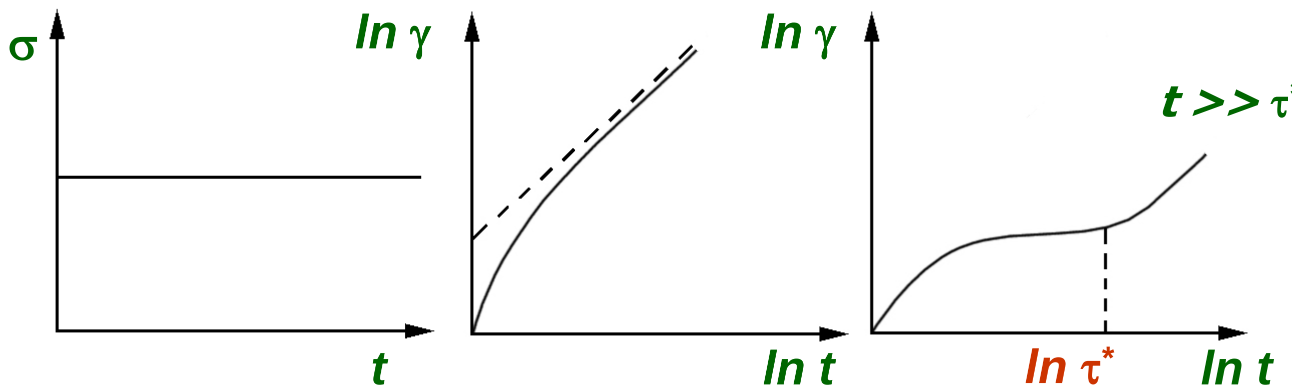


$$f = \eta \frac{S\upsilon}{d}$$

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

Viscosity: proportionality coefficient η

Viscoelasticity?



Step-wise stress starting at $t = 0$

normal liquid

polymer

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

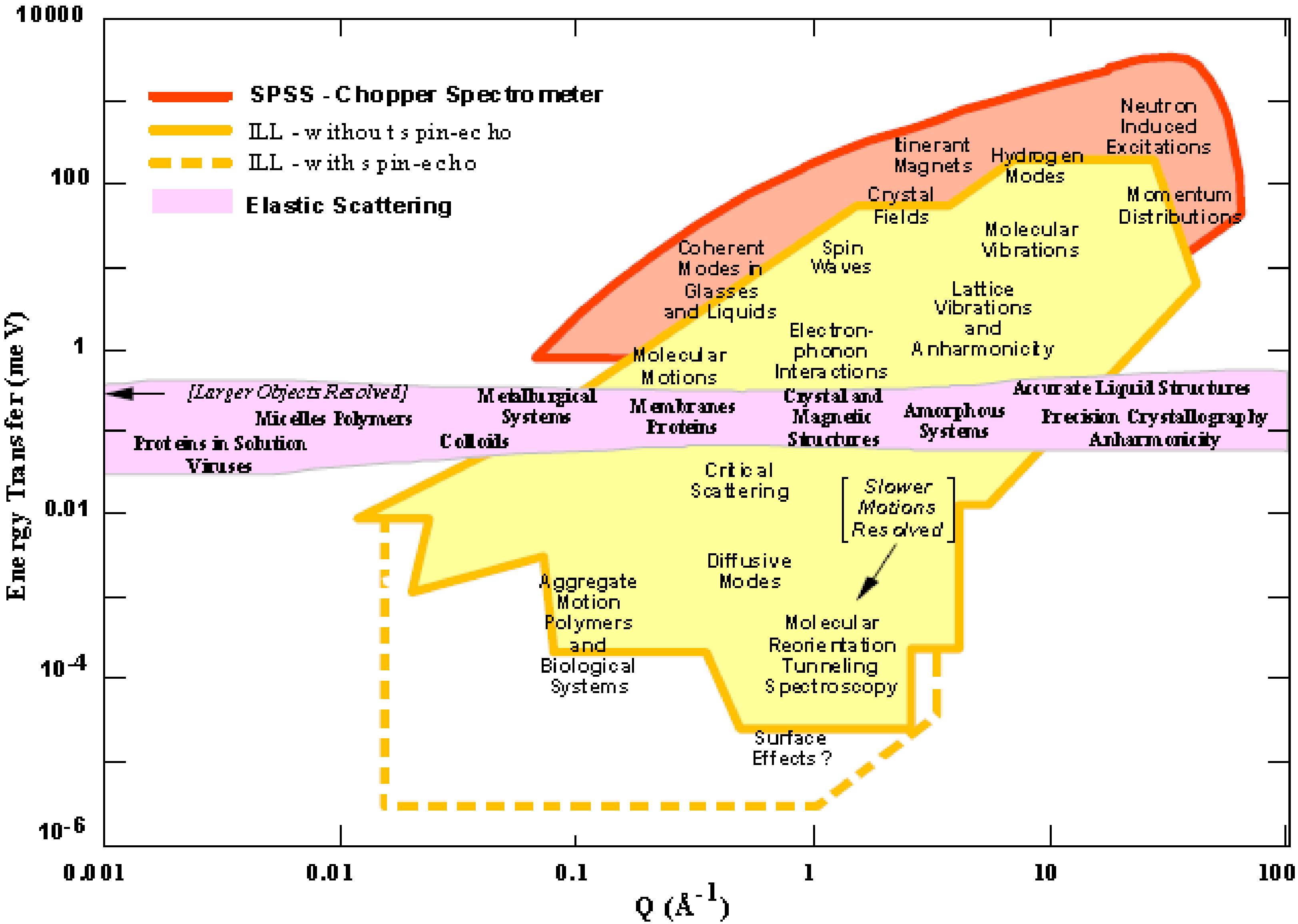
$$\gamma \approx \sigma / E$$

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

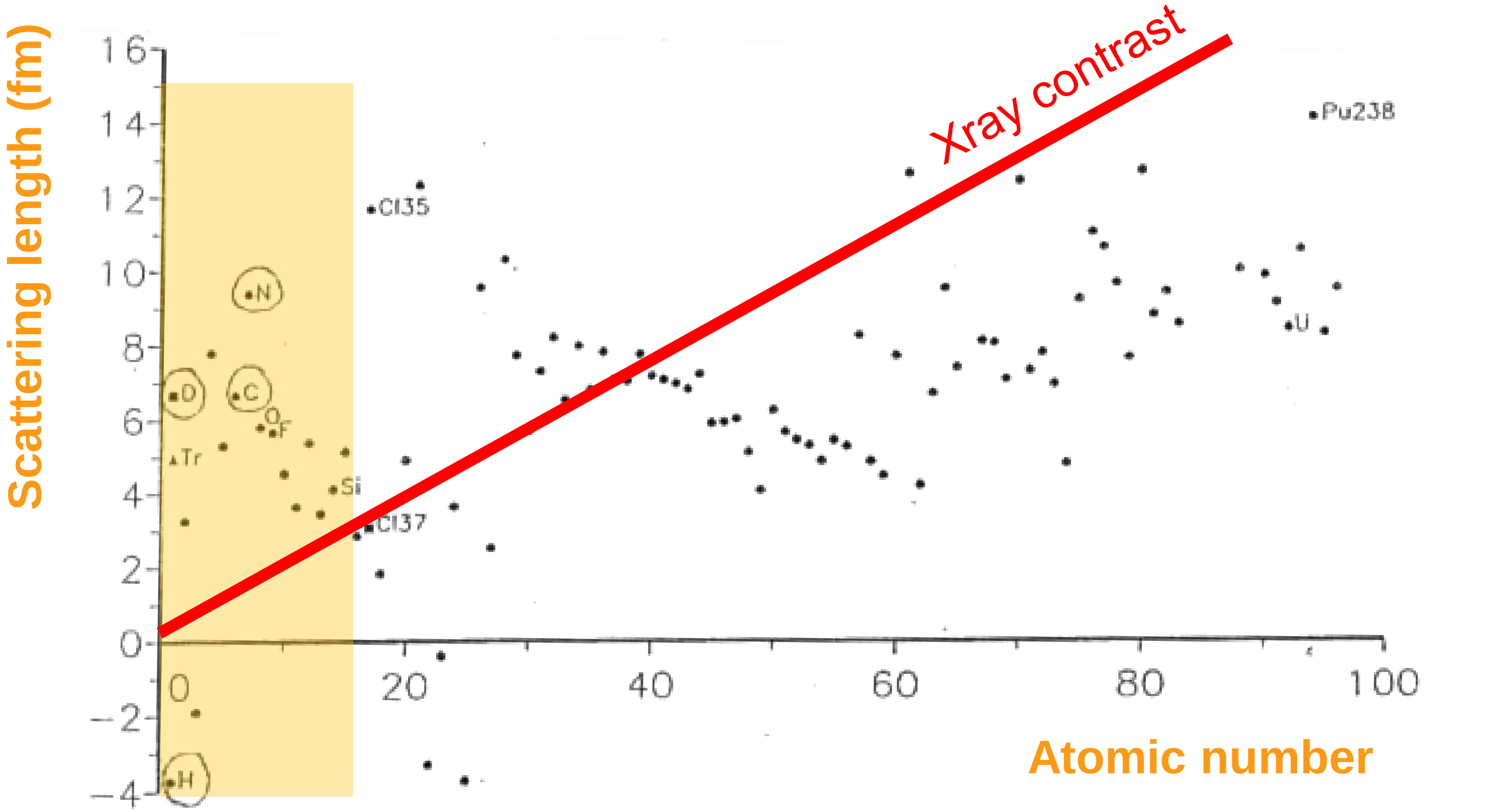
$$\gamma \propto \sigma \cdot t / \eta$$

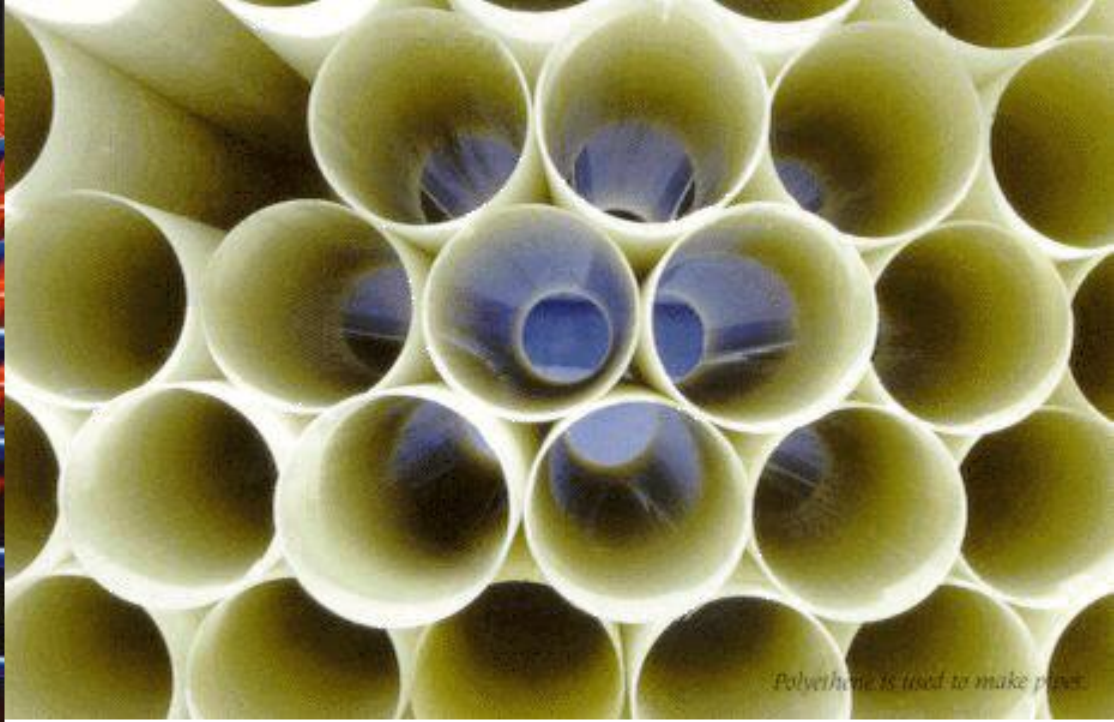
γ **shear angle**

Neutron scattering is *key* in soft condensed matter

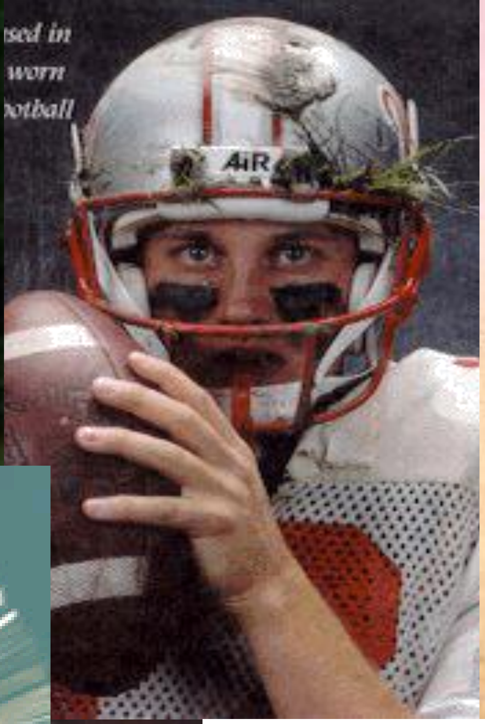


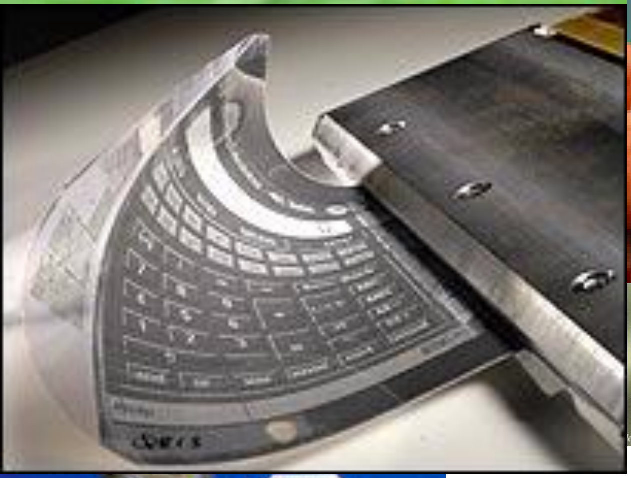
Neutron scattering is *key* in soft condensed matter

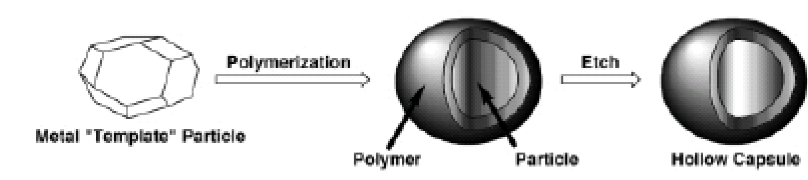




Common soft matter



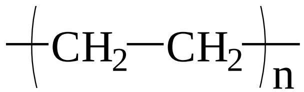




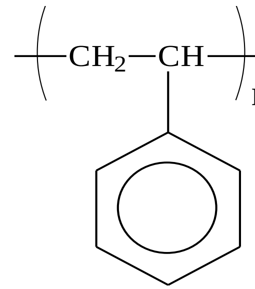
Speciality polymers

Common polymers

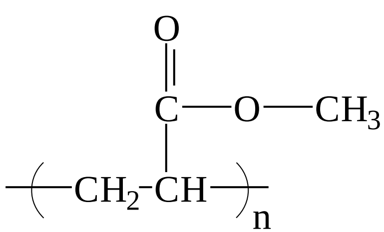
PE poly(ethylene)



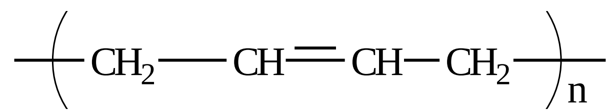
PS poly(styrene)



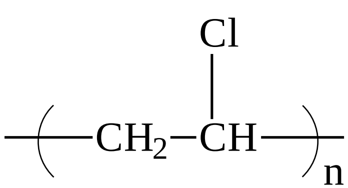
PMMA
poly(methylmethacrylate)



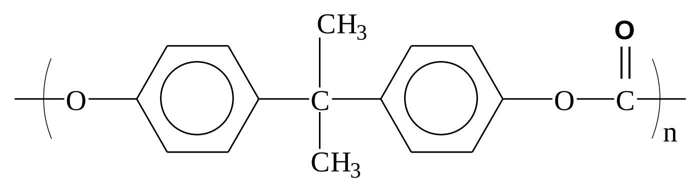
PB poly(butadiene)



PVC poly(vinylchloride)

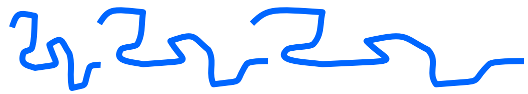


BPA-PC bisphenol-A
polycarbonate

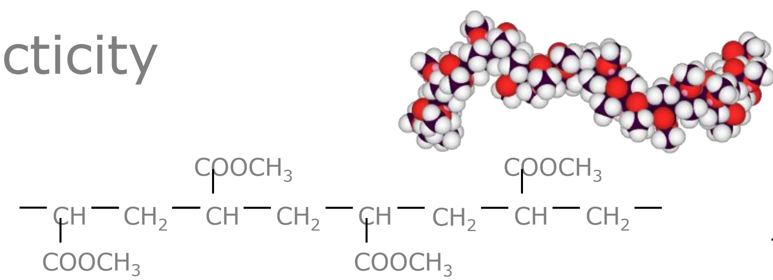


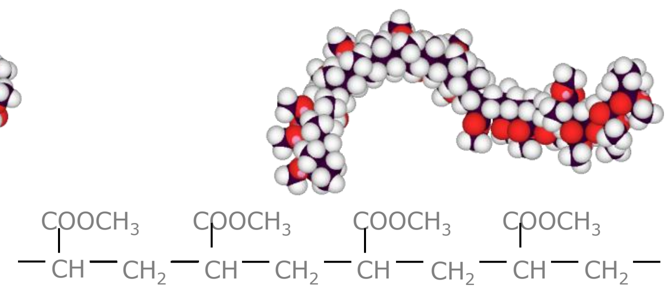
Polymer key properties

Molecular weight, N  (size)

Polydispersity  (distribution of sizes)

Tacticity



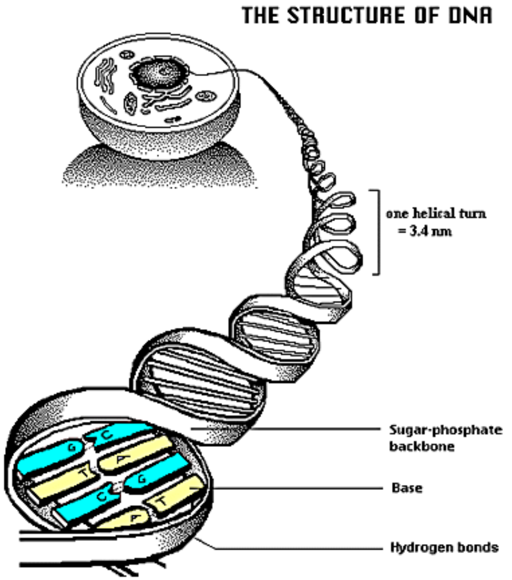


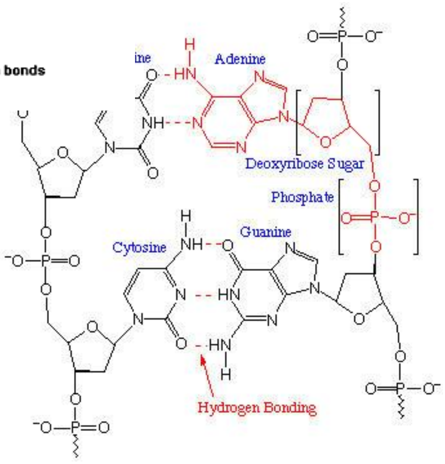
Glass transition (solid-liquid)

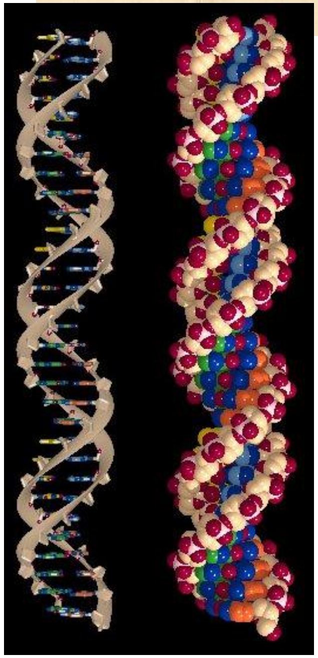
Crystallinity

Interaction parameter χ → Combine properties to make new materials!

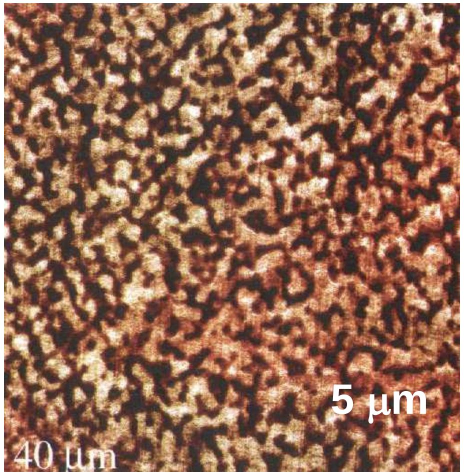
Soft matter: DNA



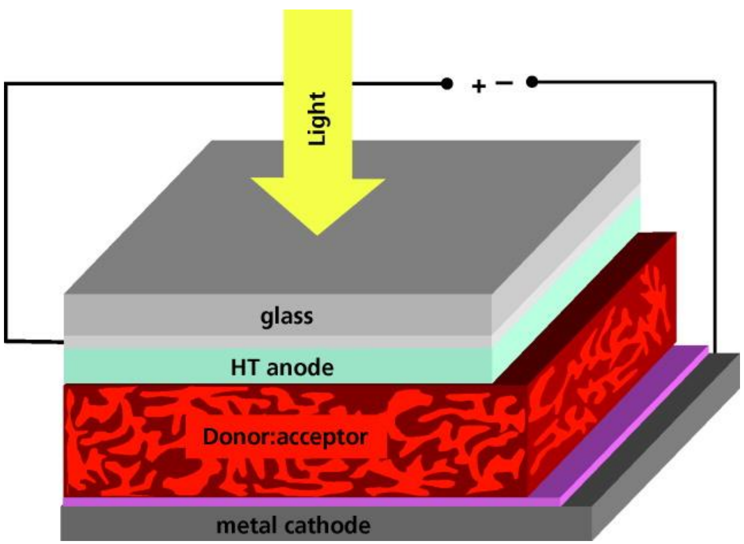


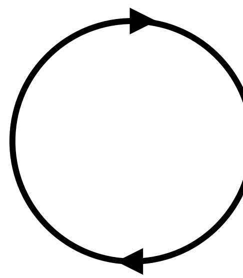


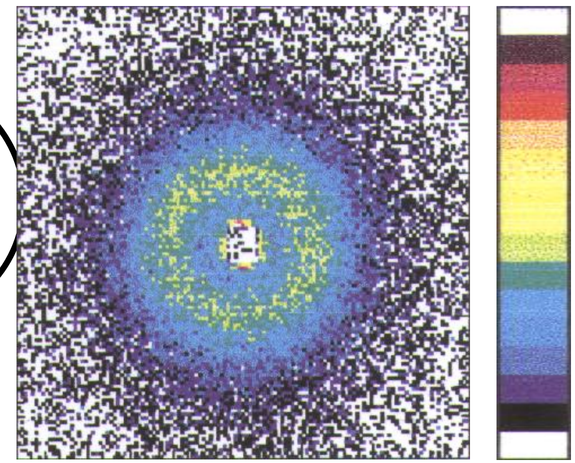
Soft Matter: membranes, photovoltaics (BHJ)



Real space

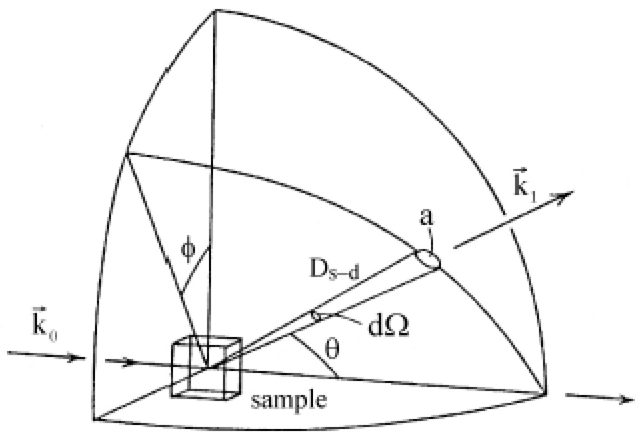






Reciprocal space

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

Reminder: Fourier Transforms

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

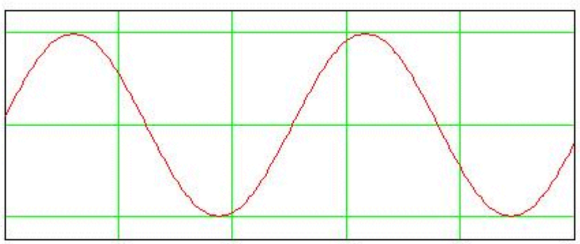
$$h(t) = \int_{-\infty} H(t)\, e^{-2\pi i f t}\, df$$

Fourier transform:

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

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

h(t)

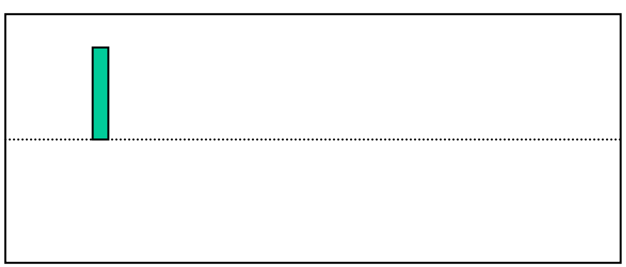


t

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

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

H(f)



f

$H(f) = 0$ if $(ft \neq 1)$

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

Reminder: Fourier Transforms

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

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

Fourier transform:

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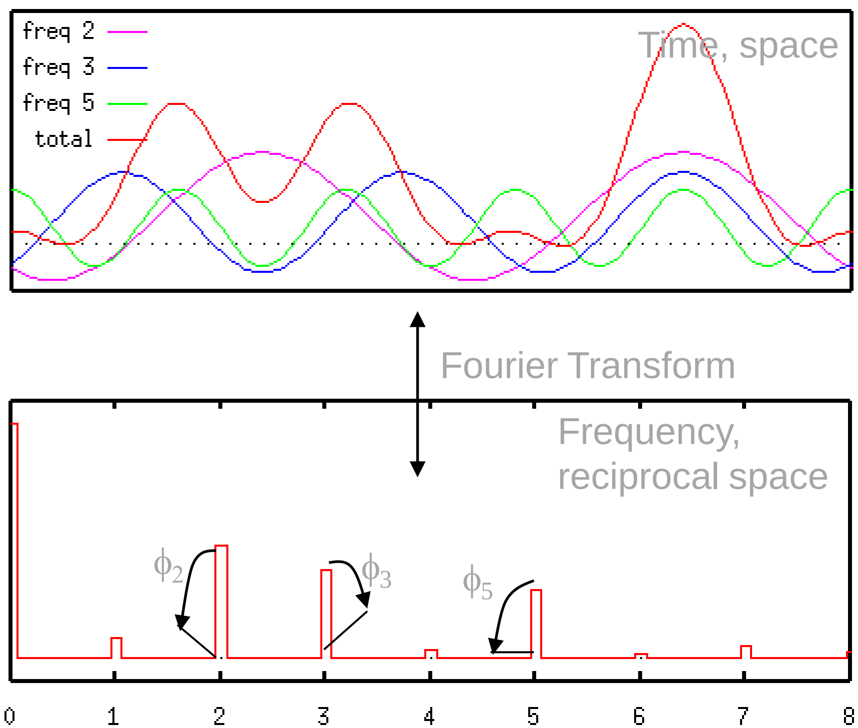
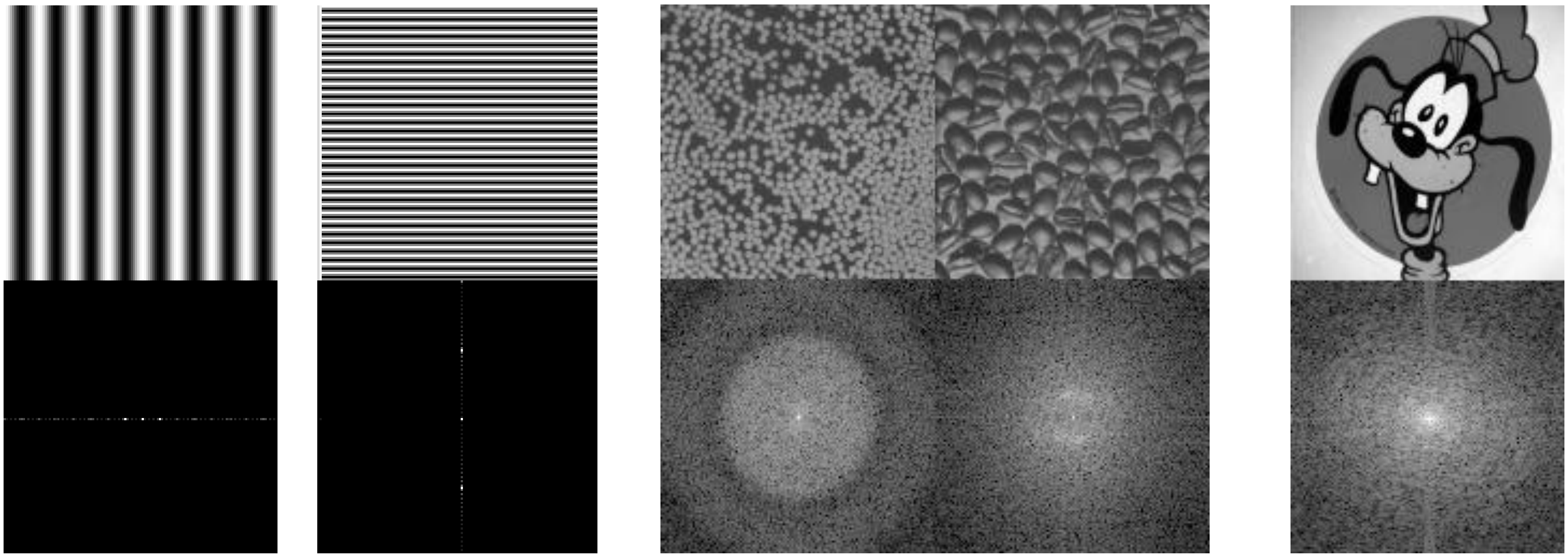


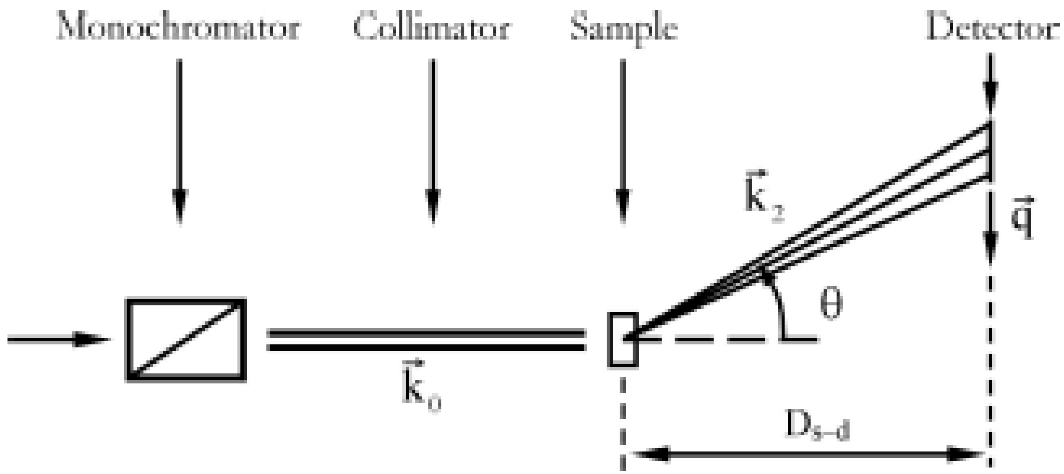
Reminder: Fourier Transforms

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

form factor

number density

contrast

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 ~ large d [large q ~ small d]

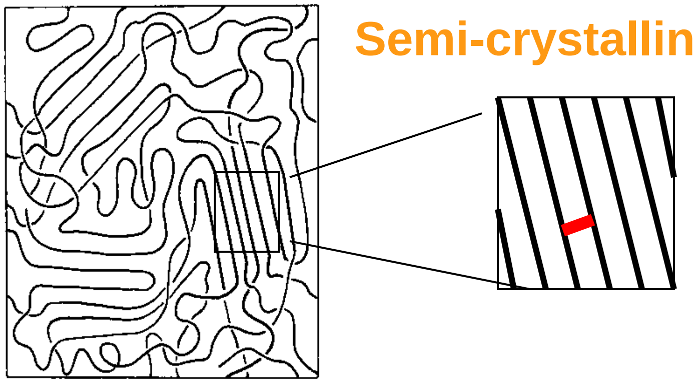
small λ ~ large q ~ small d
[large λ ~ small q ~ large d]

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

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

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 ~ 20 nm

q = 2π/d ~ 0.3 nm^{-1}

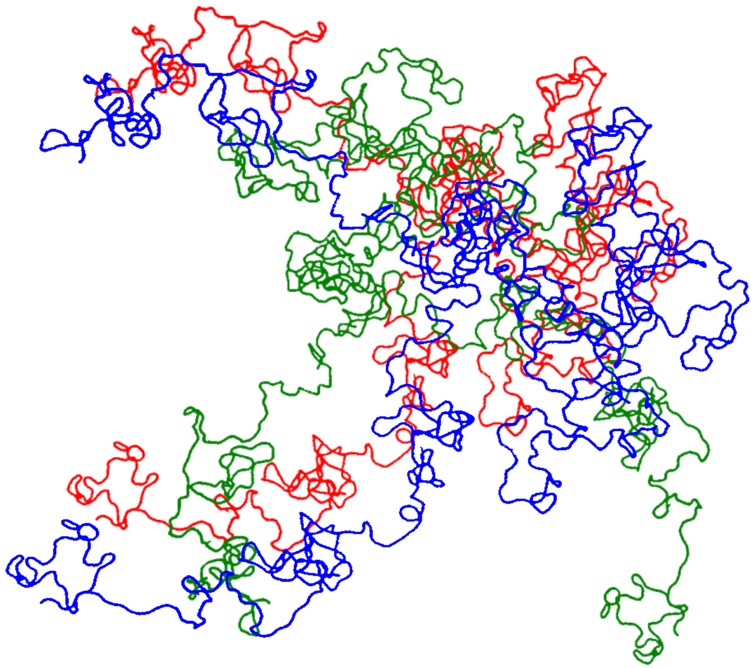
$$q = \frac{4\pi}{\lambda}\sin(\theta/2)$$

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. ⇒ **no freedom of independent motion (unlike systems of disconnected particles, e.g. low molecular gases and liquids).** ⇒ **Polymer systems are *poor in entropy*.**

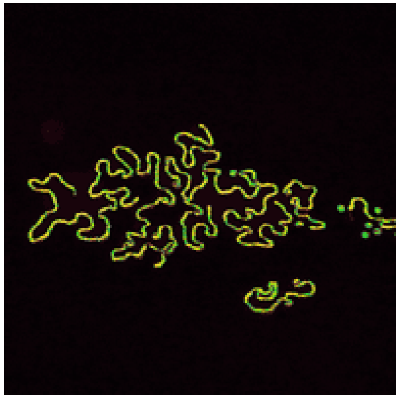
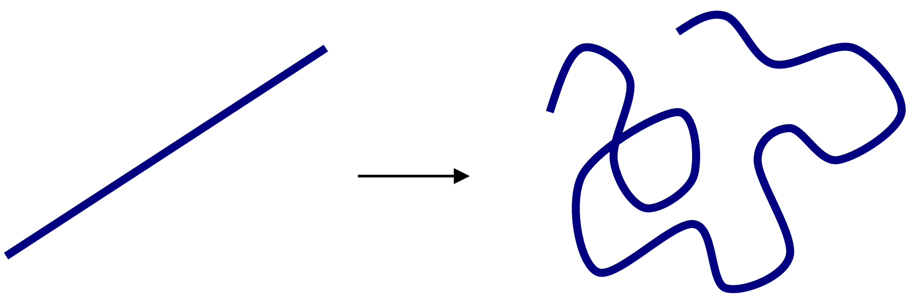


Image single molecule (AFM) Magonov

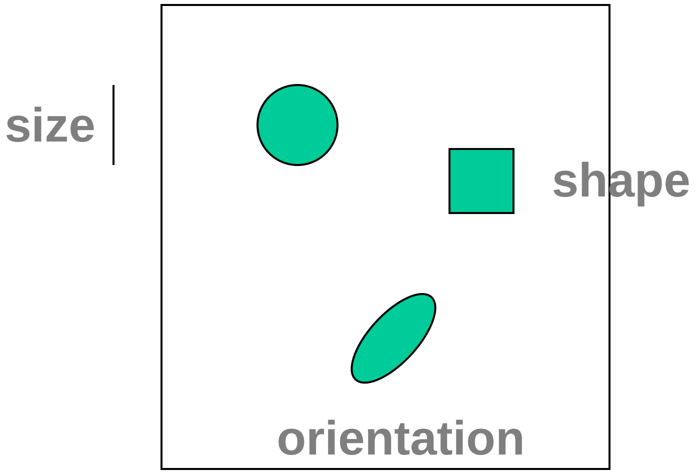
3. Polymer chains are generally *flexible*.



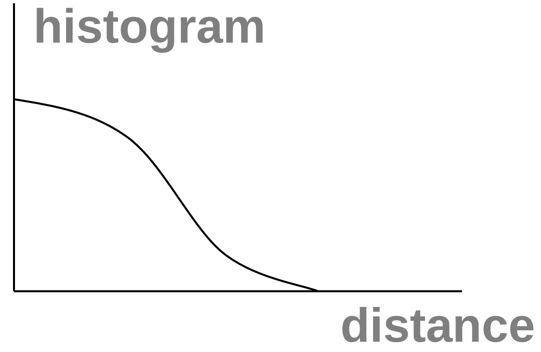
Form factor: P

Self-correlations

Form factor *P*



'sample'

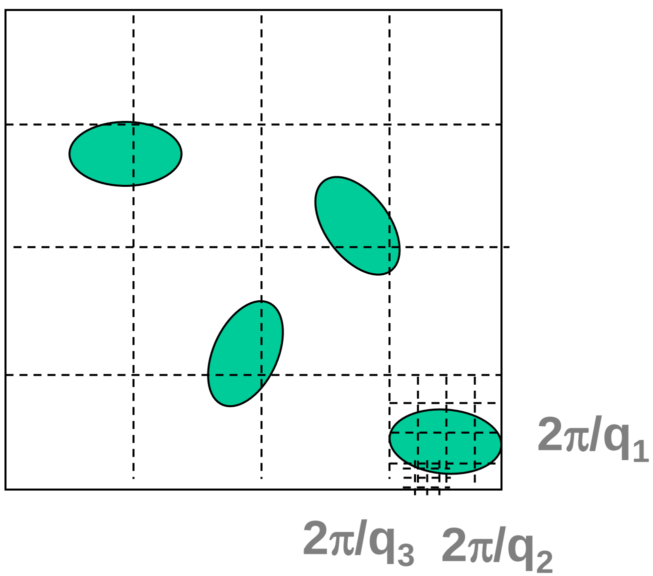


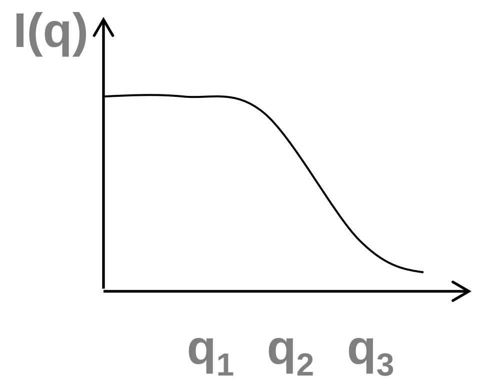
$$P(Q) = \frac{1}{V_p^2} \left| \int_0^{V_p} \exp\left[i \; f(Q \, \alpha) \right] \, dV_p \right|$$

Interference between scattered radiation from different parts of the same object

(analytical solutions for common shapes)

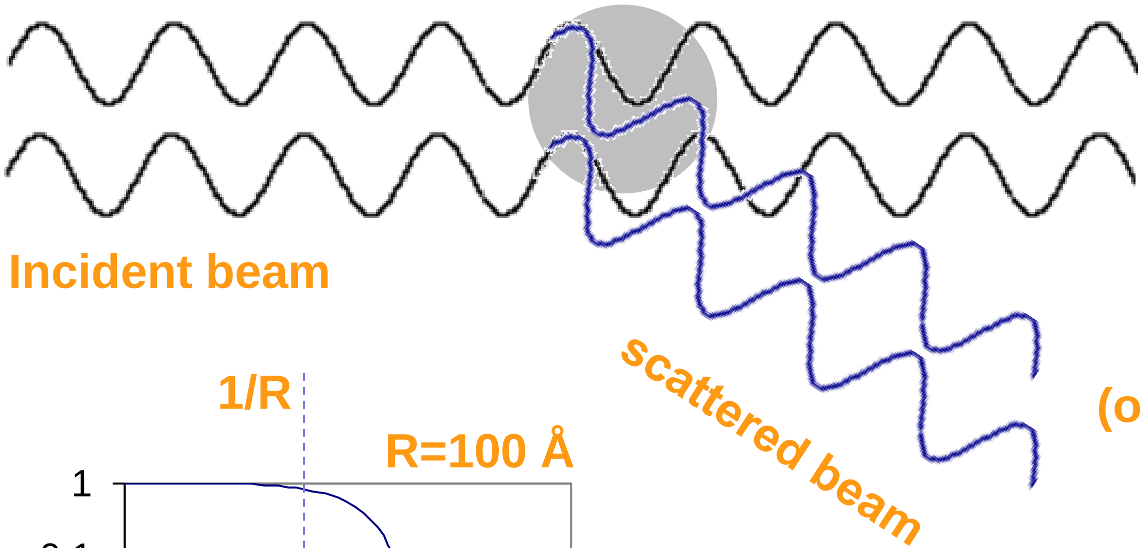
Multiple lengthscales

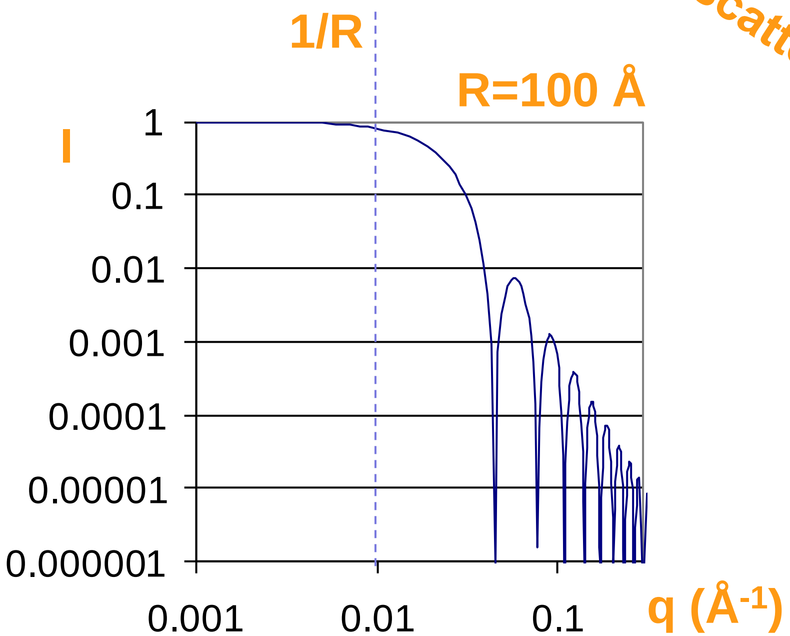




scattering spectrum corresponds to different “magnifications”, thus several approximations may be relevant

Scattering from a sphere

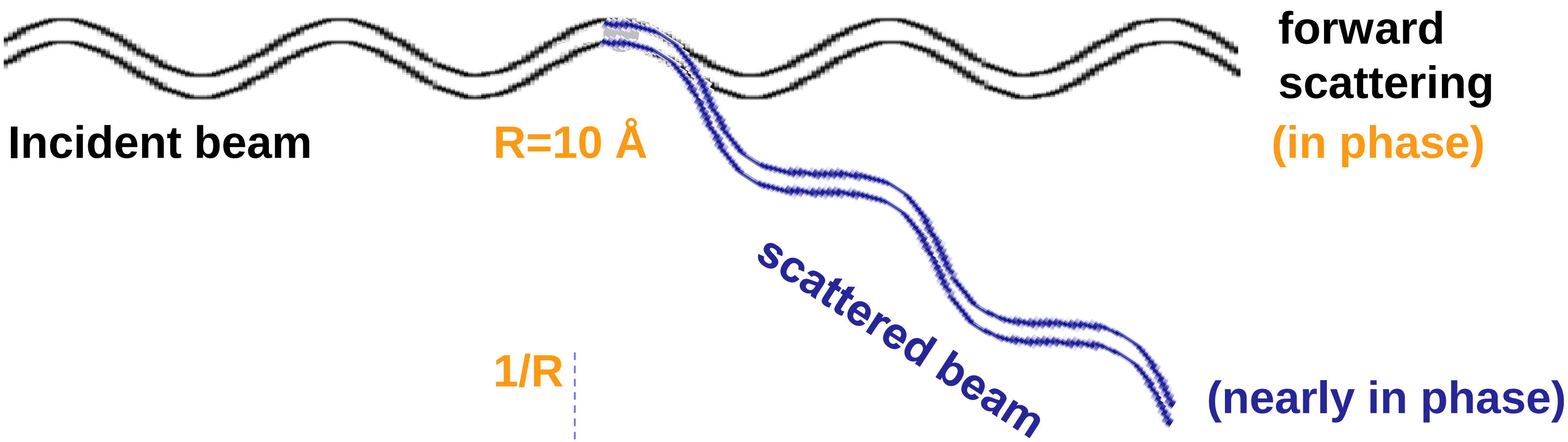


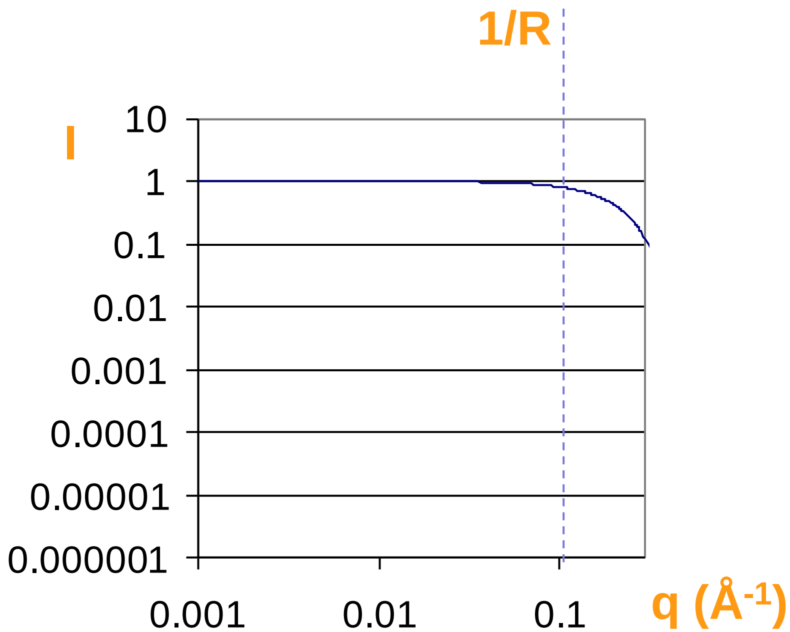


$$P(q) = \frac{9\left(\sin qR - qR\cos qR\right)^2}{\left(qR\right)^6}$$

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

Scattering from a (tiny) sphere

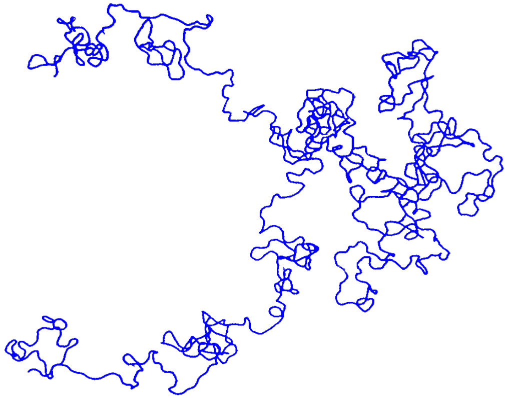




$$P(q) = \frac{9\left(\sin qR - qR\cos qR\right)^2}{\left(qR\right)^6}$$

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

Scattering from a random coil



Debye form factor

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

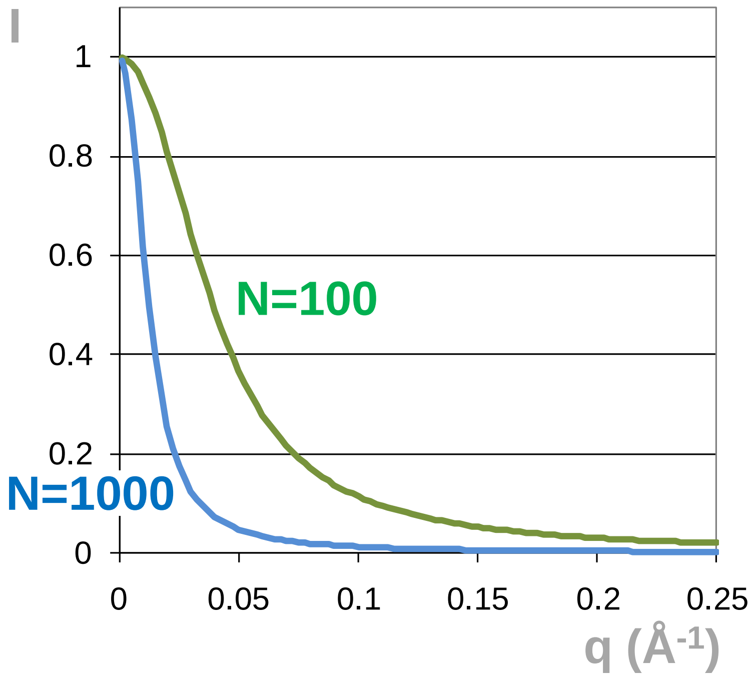
$$x \equiv q^2 R_g^2$$

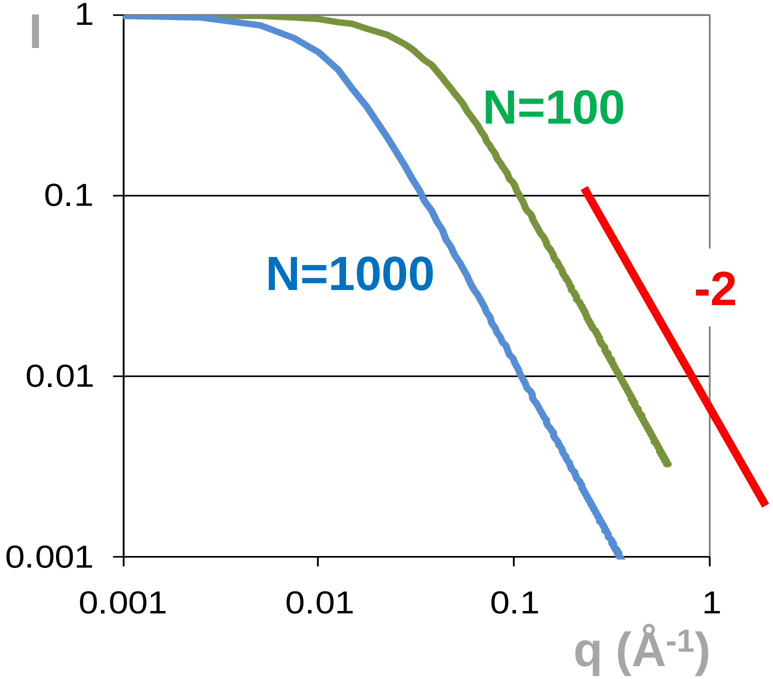
$$R_g^2 = \frac{Na^2}{6}$$

a=10 Å

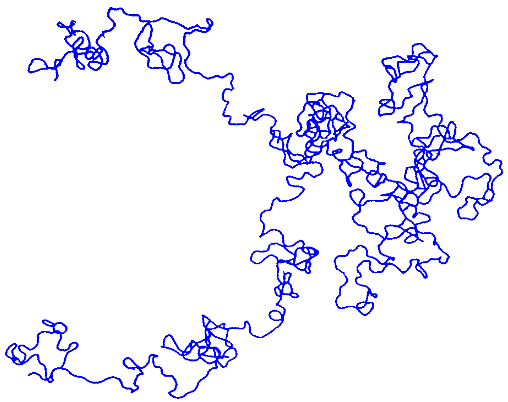
N=100 → Rg≈4nm

N=1000 → Rg≈13nm





Scattering from a random coil



Debye form factor

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

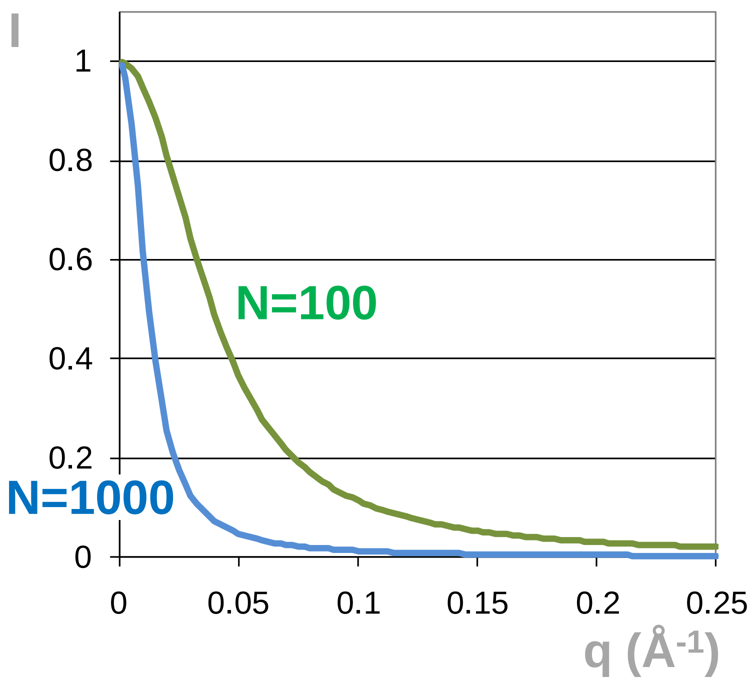
$$x \equiv q^2 R_g^2$$

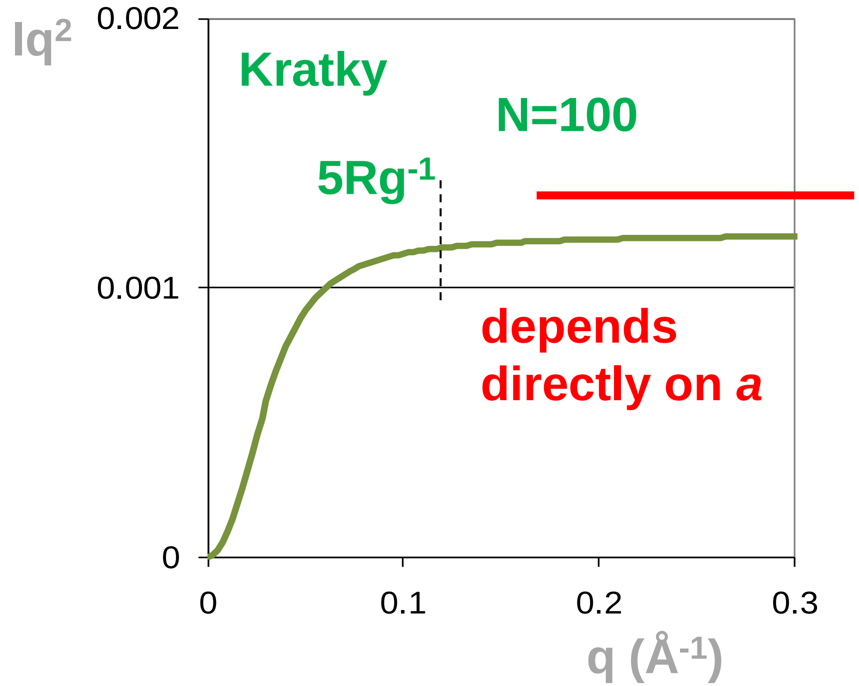
$$R_g^2 = \frac{Na^2}{6}$$

a=10 Å

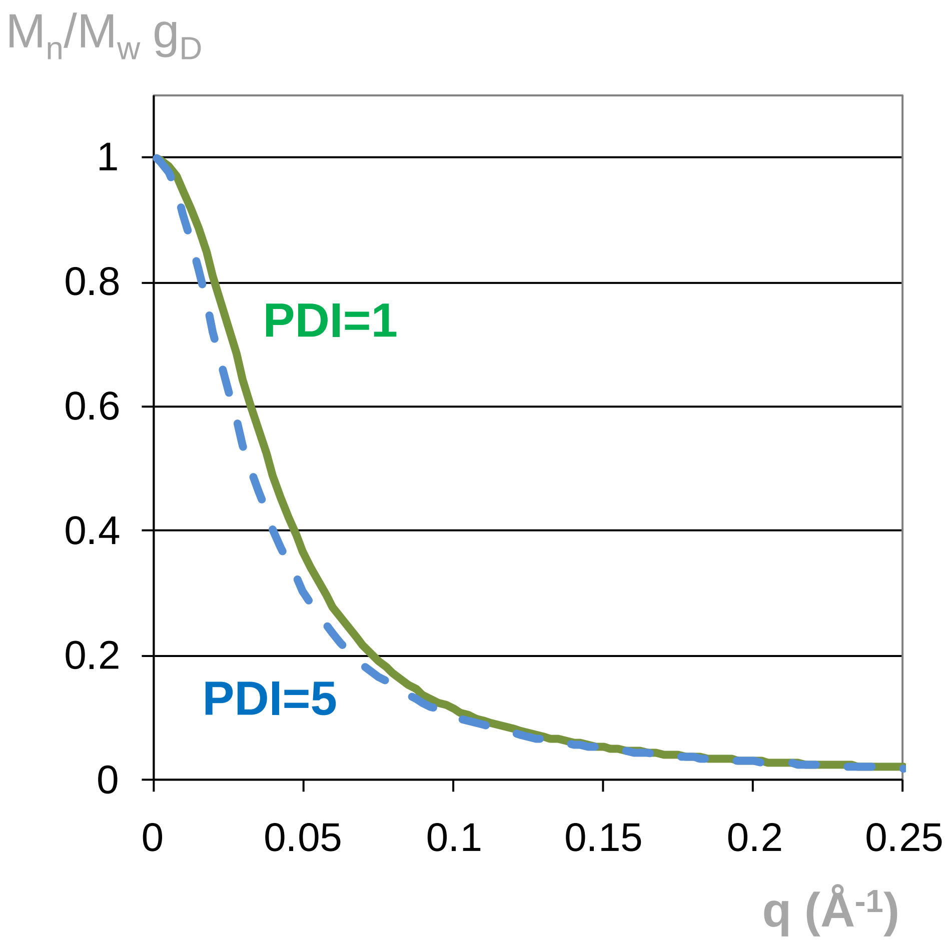
N=100 → Rg≈4nm

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

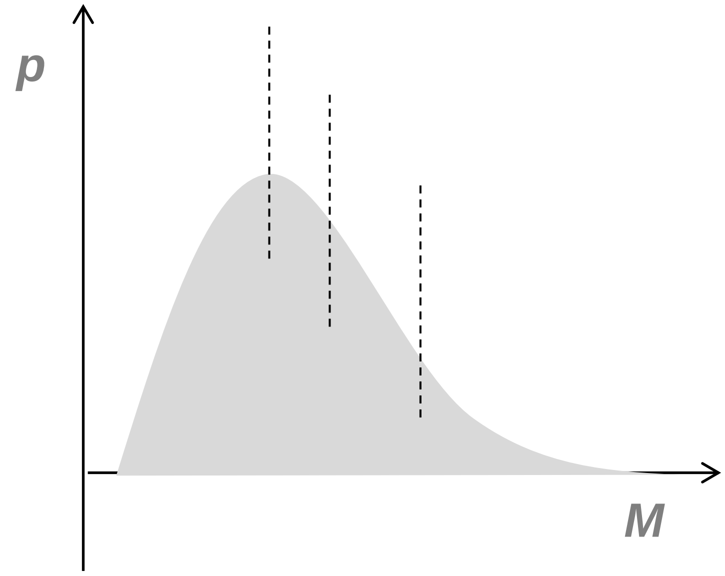
N_w=100, N_w/N_n=5

A polydispersity model

(Schultz-Zimm)

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

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

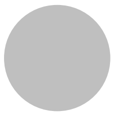


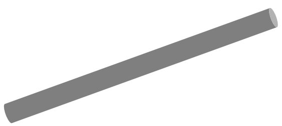
Number average $M_n = \int p(M) M \, dM$

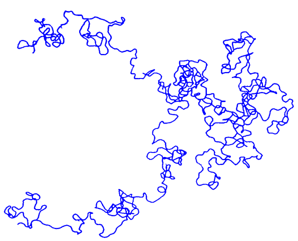
Weight average $M_w = \frac{\int p(M) M^2 dM}{\int p(M) M \, dM} \equiv \frac{\langle M \rangle_2}{\langle M \rangle_1}$

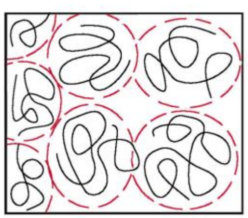
$\mathrm{z} - \mathrm{average}$ $M_z = \frac{\int p(M) M^3 dM}{\int p(M) M^2 dM} \equiv \frac{\langle M \rangle_3}{\langle M \rangle_2}$

Useful form factors







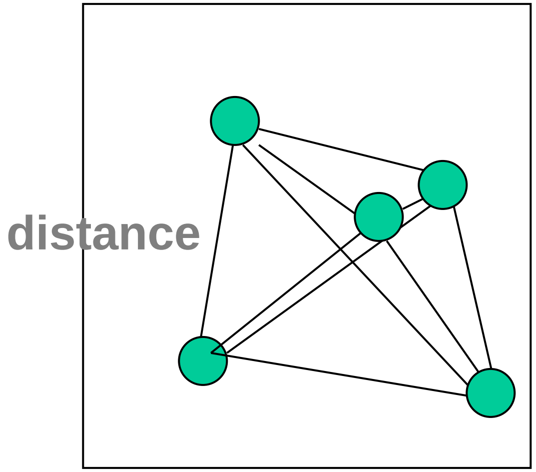


Sphere of radius R_p	$P(Q) = \left[\frac{3\,(Sin\,(QR_p) - QR_p\;Cos\,(QR_p))}{(QR_p)^3}\right]^2$
Disc of negligible thickness and radius R_p (J_1 is a first-order Bessel function)	$P(Q) = \frac{2}{(QR_p)^2}\left[1 - \frac{J_1(2QR_p)}{QR_p}\right]$
Rod of negligible cross-section and length L (S_i is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

S King

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

Structure factor: S

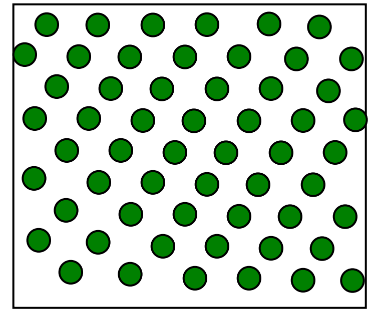


Interference between radiation scattered by distinct objects

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

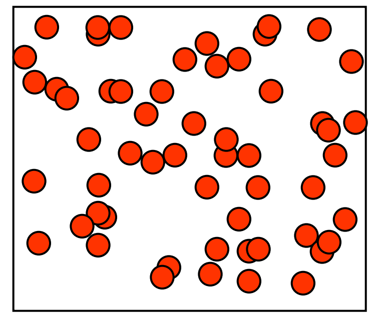
$$G(r) = \frac{4\pi N_p r^2}{V} g(r)$$

Radial distribution function, provides information about their relative position

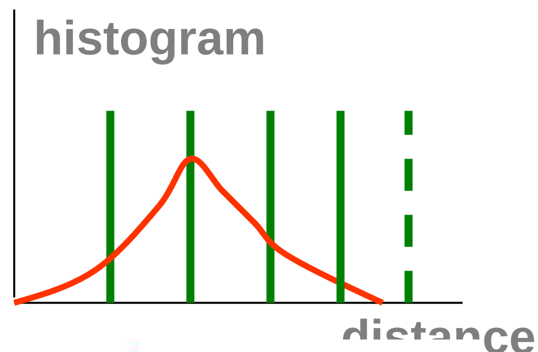


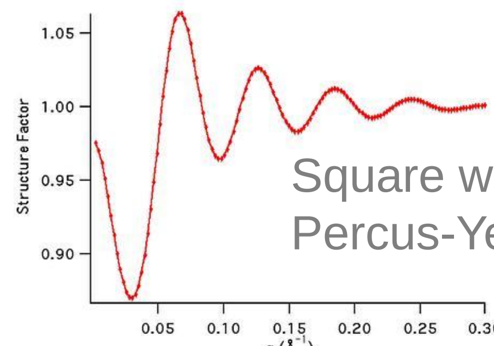
Ordered structure

'crystal'



Disordered structure

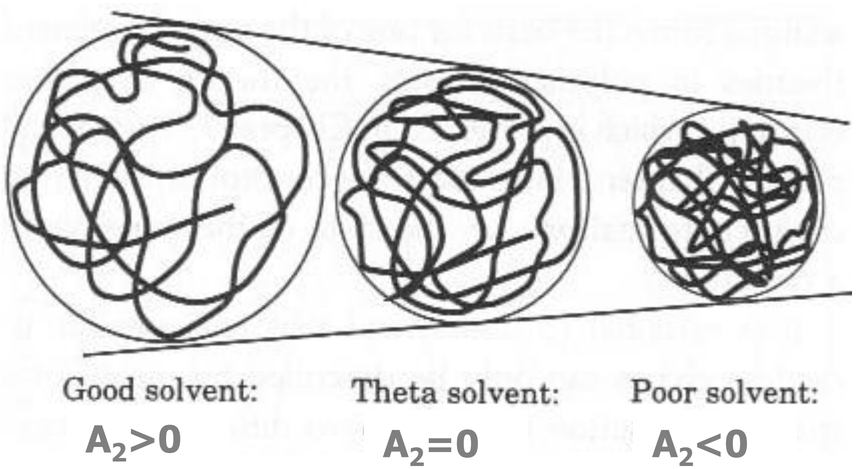


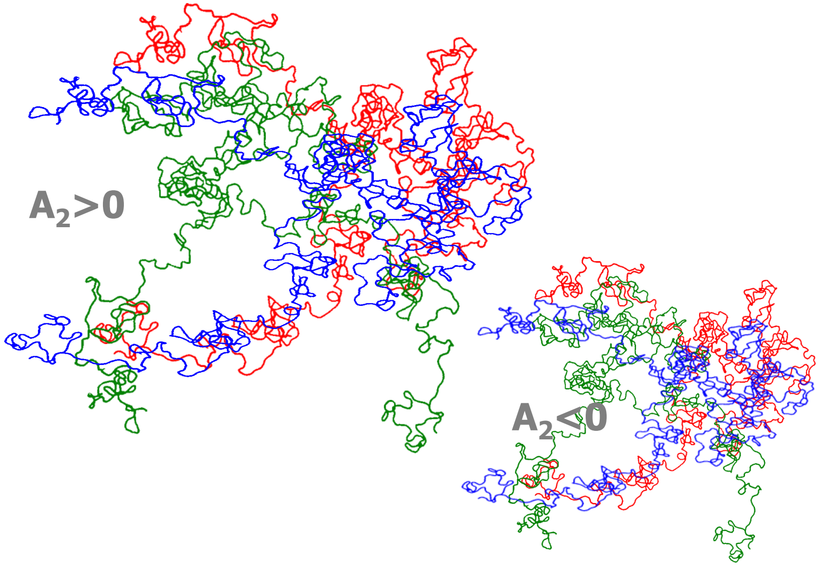


Square well, Percus-Yevick...

Interactions: Polymers in solution and melt

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

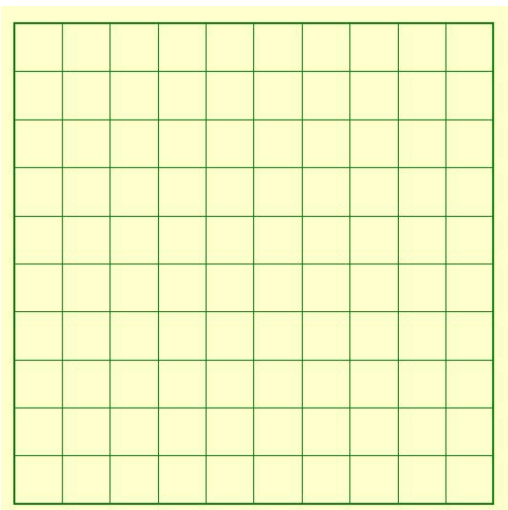




Ideal chains occur in θ-solutions (ie, neutral solvent, $A_2=0$) or in melt. Chains expand or contract depending on interactions: A_2 (Second Virial coeff, for solutions) or χ (for polymer mixtures)

Polymer miscibility (1)

***Flory-Huggins* lattice**



Binary mixture

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

Combinatorial entropy

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

Ω Boltzmann law

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

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

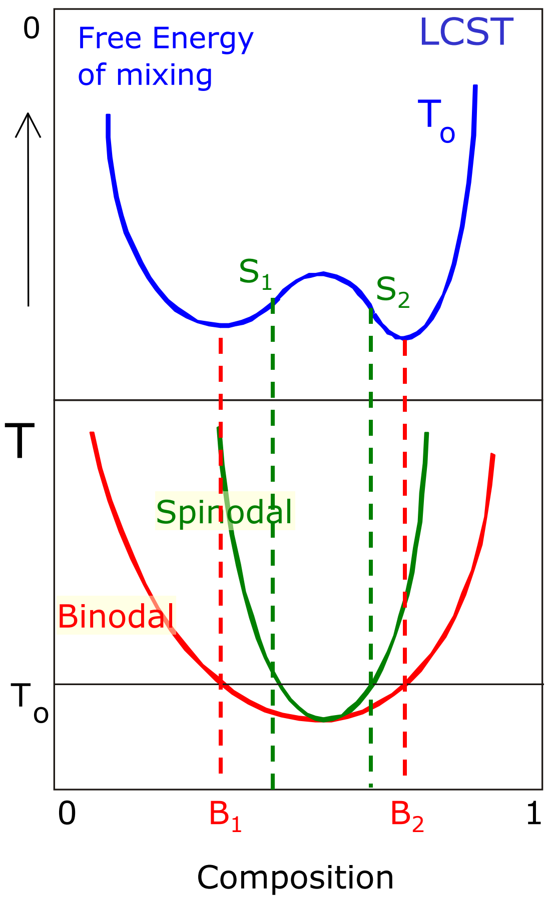
Combinatorial entropy

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

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

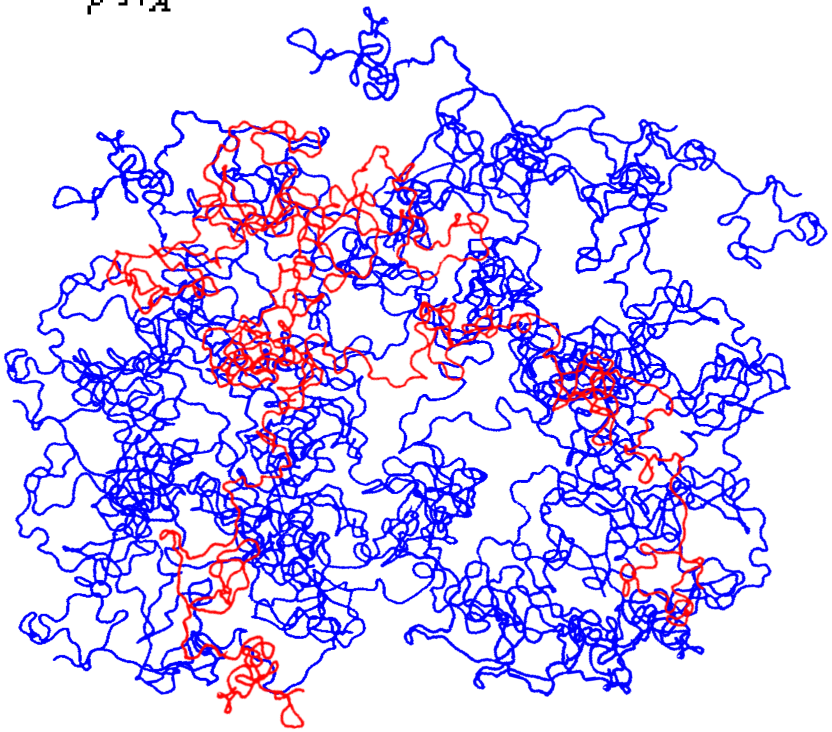
inflection points

Isotopic polymer mixture

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

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

$$= (b_D - b_H)^2\,\phi(1-\phi)\,\langle M\rangle_w\,\frac{(\Delta\varrho)^2}{\rho\,N_A}\,P(q)$$



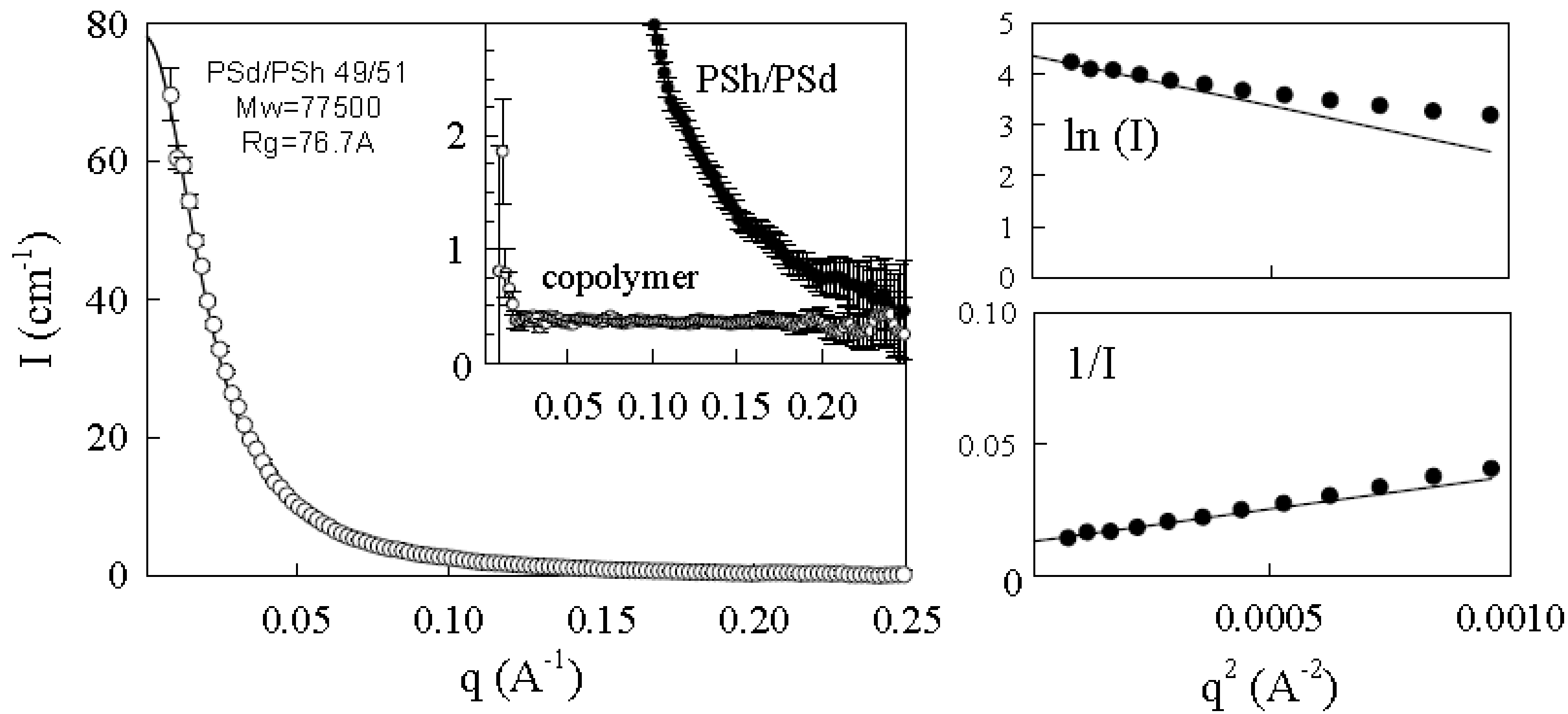
Approximations: Guinier & Zimm

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

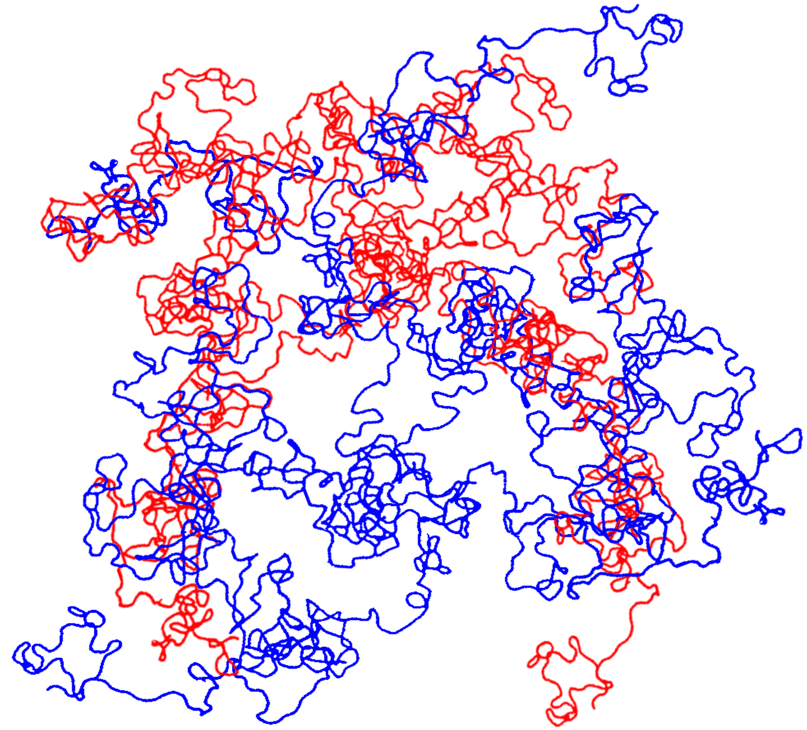
$$\text{Zimm}: \quad \left[\frac{d\Sigma(q)}{d\Omega}\right]^{-1} \approx \left[\frac{d\Sigma(0)}{d\Omega}\right]^{-1} \left[1 + \frac{(qR_g)^2}{3}\right]$$

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

for a polymer coil



Interacting polymer mixtures



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

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

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

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

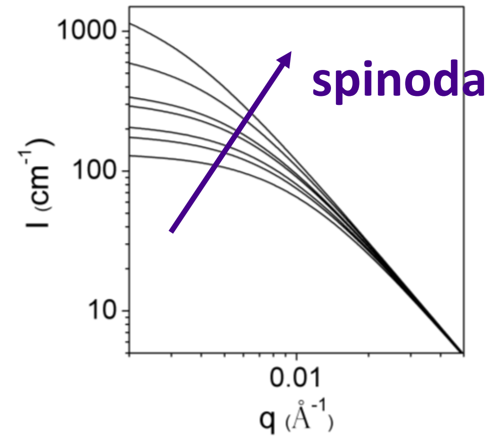
$$\frac{1}{S(0)} = \frac{1}{\phi_1 v_1 \langle N_1\rangle_w} + \frac{1}{\phi_2 v_2 \langle N_2\rangle_w} - 2\frac{\tilde{\chi}_{12}}{v_0}$$

Random Phase Approximation

RPA (de Gennes, 1979):

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

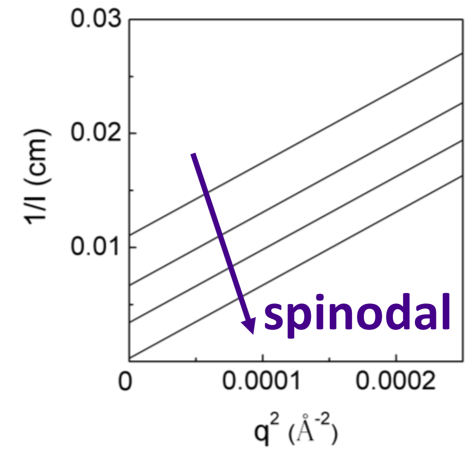
1/S(0) = G''



Ornstein-Zenike:

At low angle (qRg << 1),

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

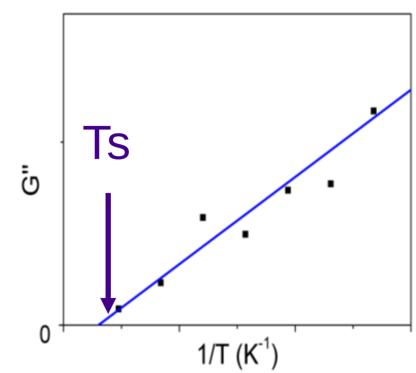


Linear in the Zimm representation as:

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

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

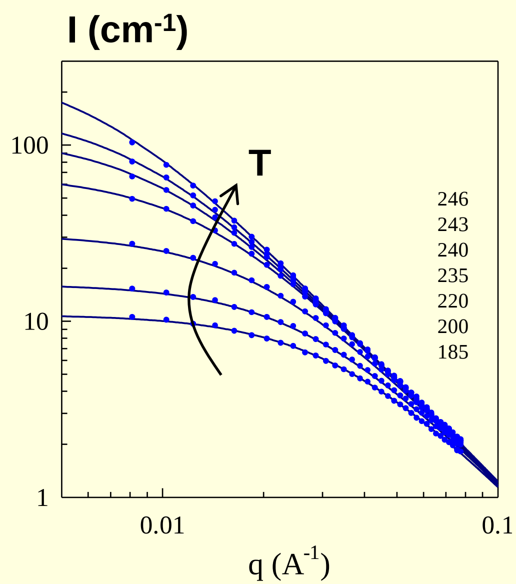
T_s determined by extrapolation of G'' to 0



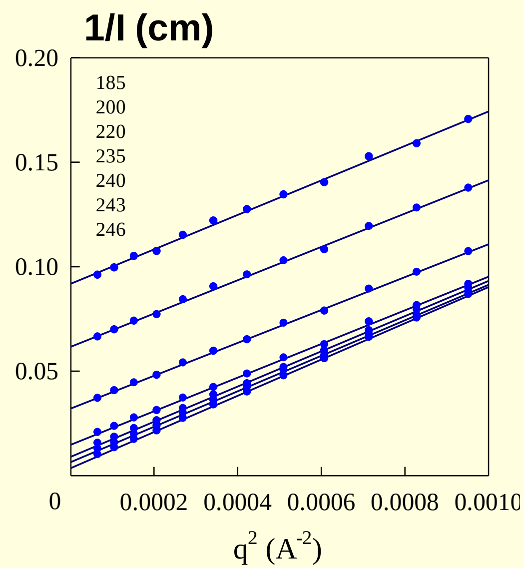
Equilibrium: SANS

TMPC/PSd 50/50

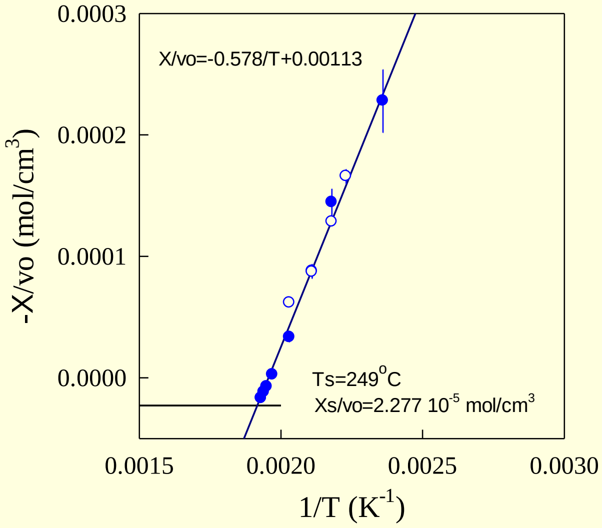
1-phase scattering



Orstein-Zernike



Interaction χFH



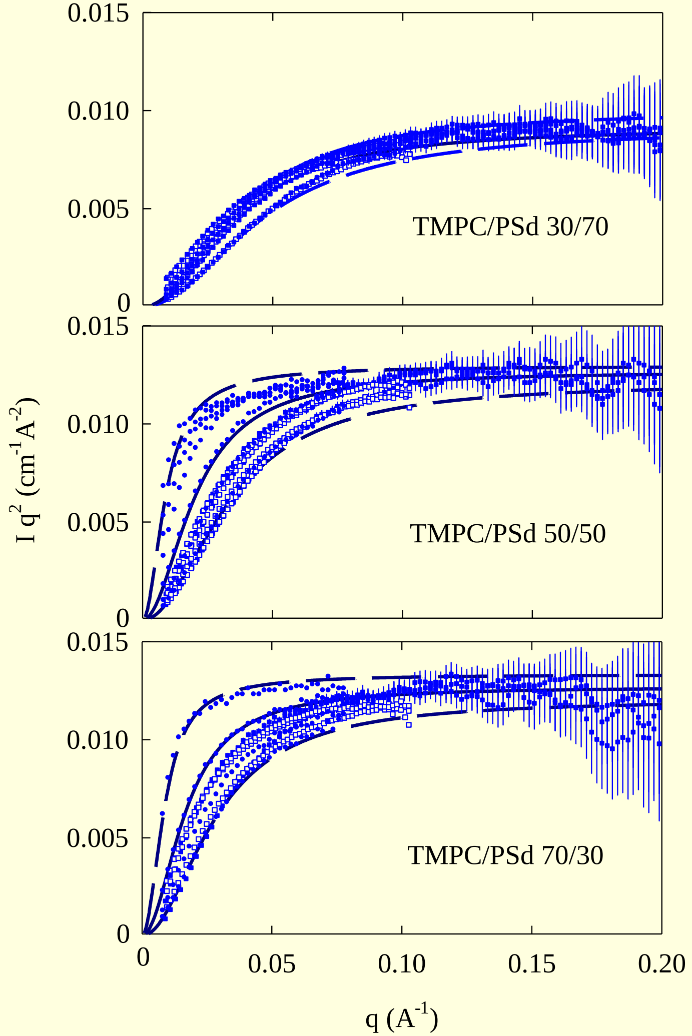
Random Phase Approximation

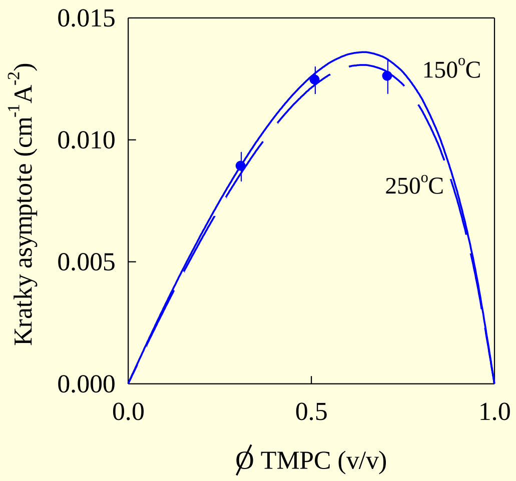
$$\frac{1}{S_{AB}(q)} = \frac{1}{\phi_A v_A \langle N_A\rangle_n \langle g_D(q)_A\rangle_w} + \frac{1}{\phi_B v_B \langle N_B\rangle_n \langle g_D(q)_B\rangle_w} - 2\frac{\tilde{\chi}_{AB}}{v_o}$$

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

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

Equilibrium: Kratky asymptote



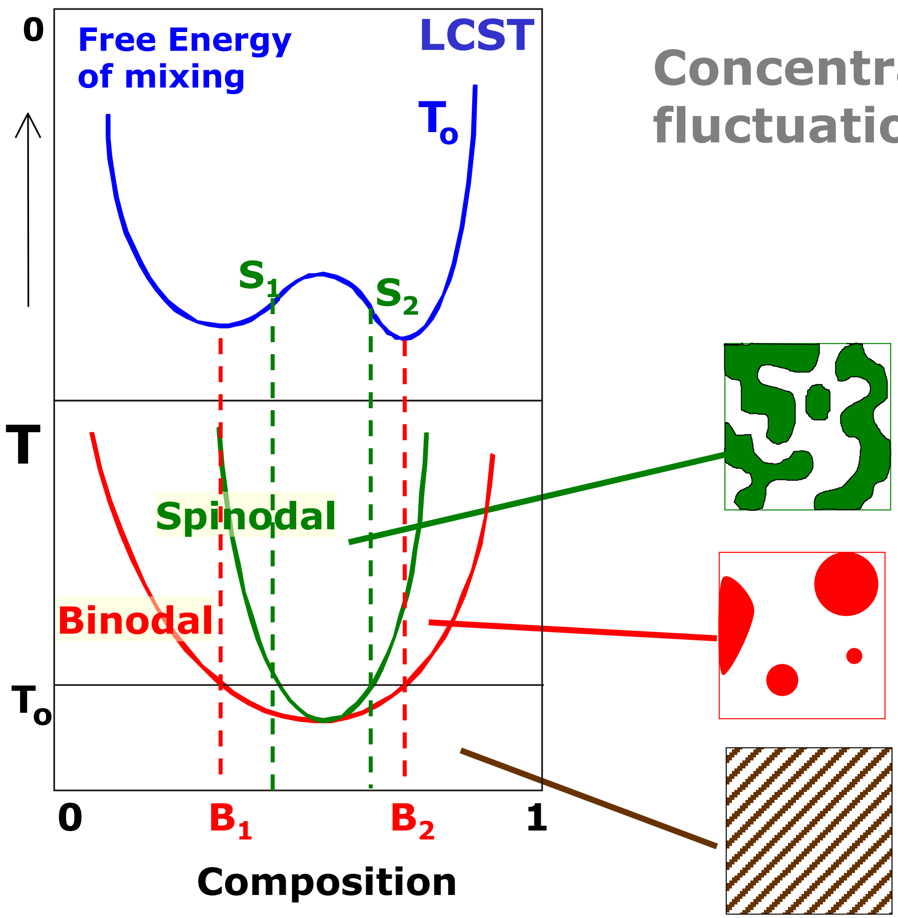


Kratky asymptote and segment length

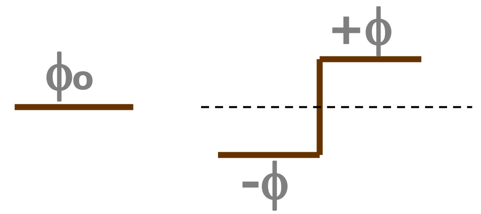
$$S(q) \approx \frac{12\phi_1\phi_2}{q^2}\frac{v_o}{\hat{a}^2}$$

$$\frac{\hat{a}^2}{v_0} \equiv \phi1\phi2\left(\frac{a_1{}^2}{\phi_1 v_1} + \frac{a_2{}^2}{\phi_2 v_2}\right)$$

Non-equilibrium: Fluctuations & Phase separation



Concentration fluctuations

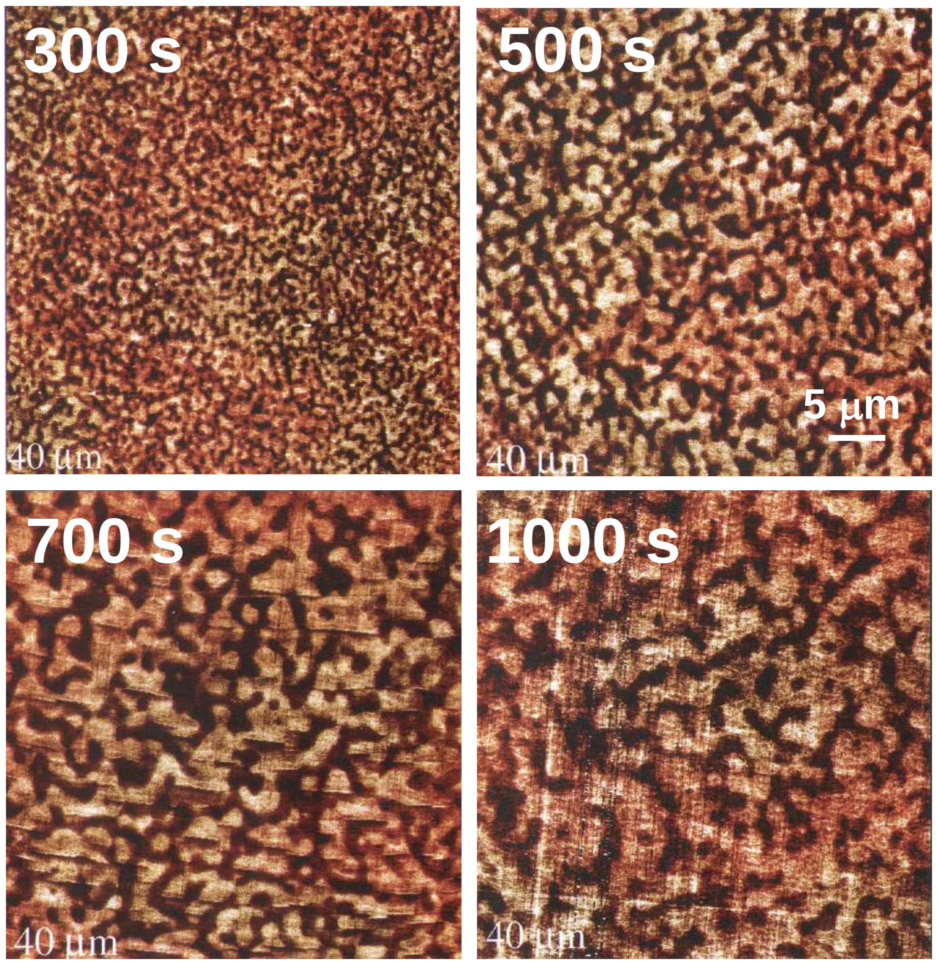


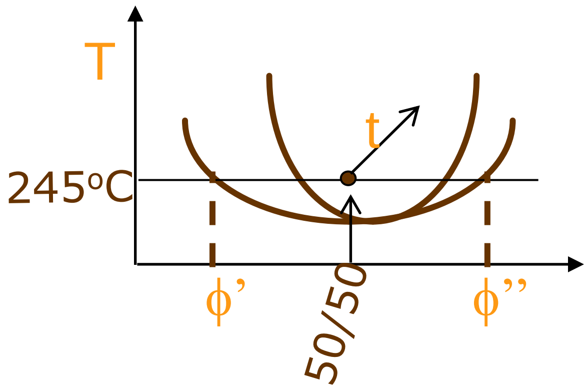
Unstable: $G'' < 0$
spinodal decomposition

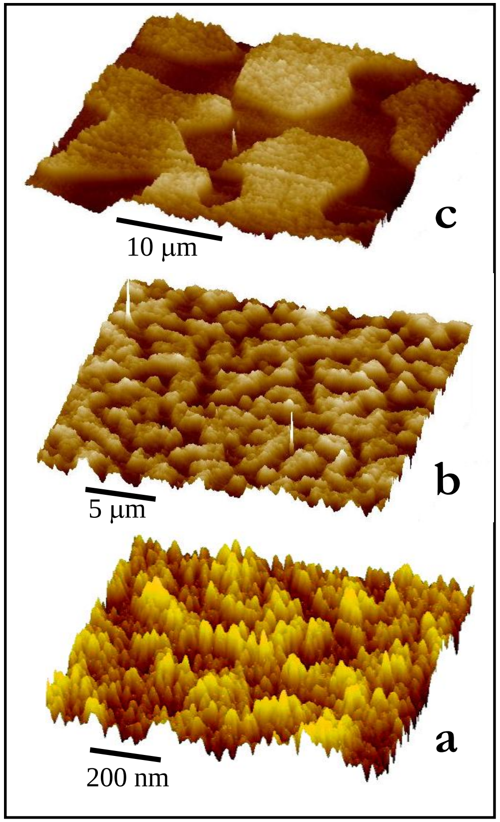
Metastable:
nucleation & growth

Stable:
equilibrium

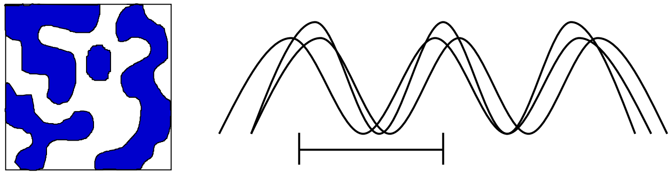
Phase separation: spinodal decomposition



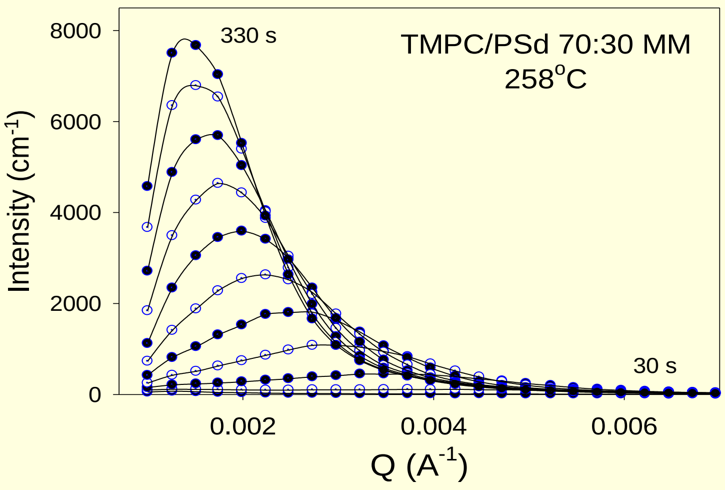


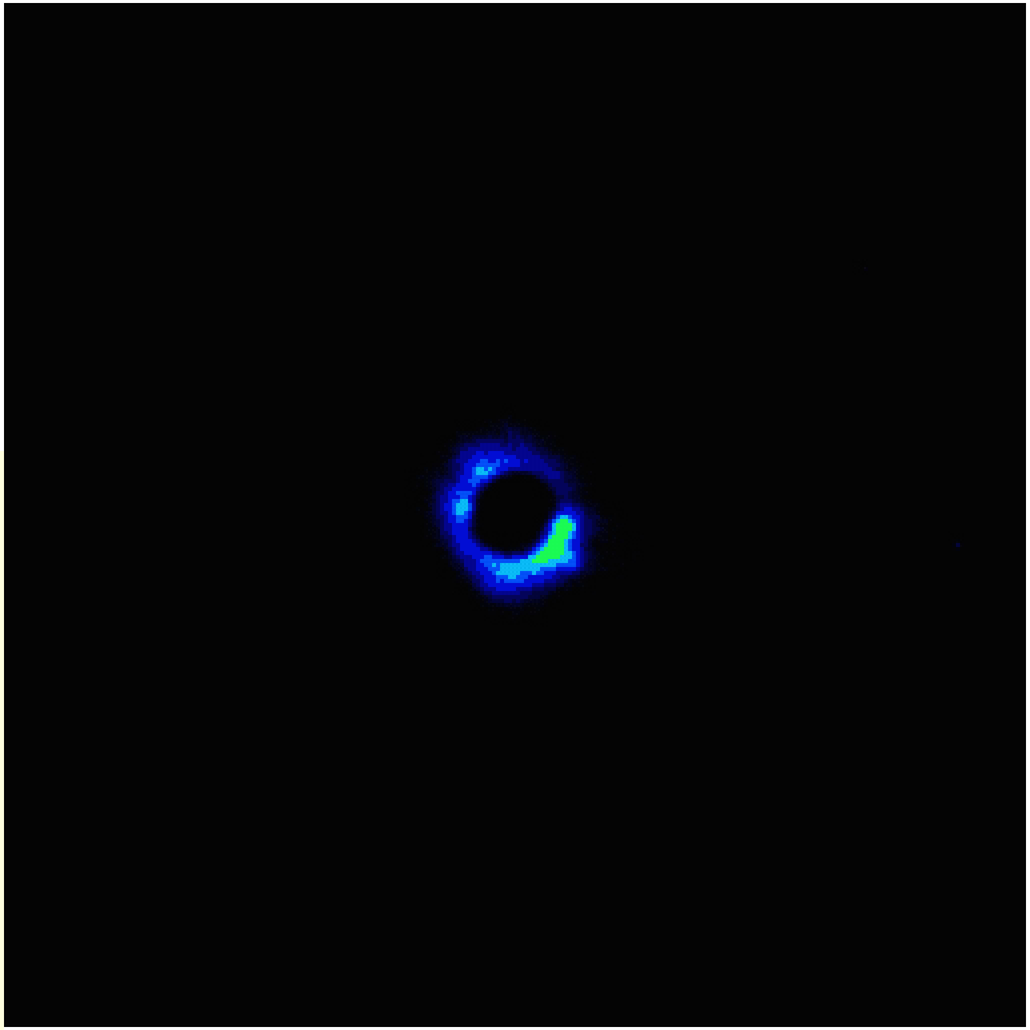


Phase separation

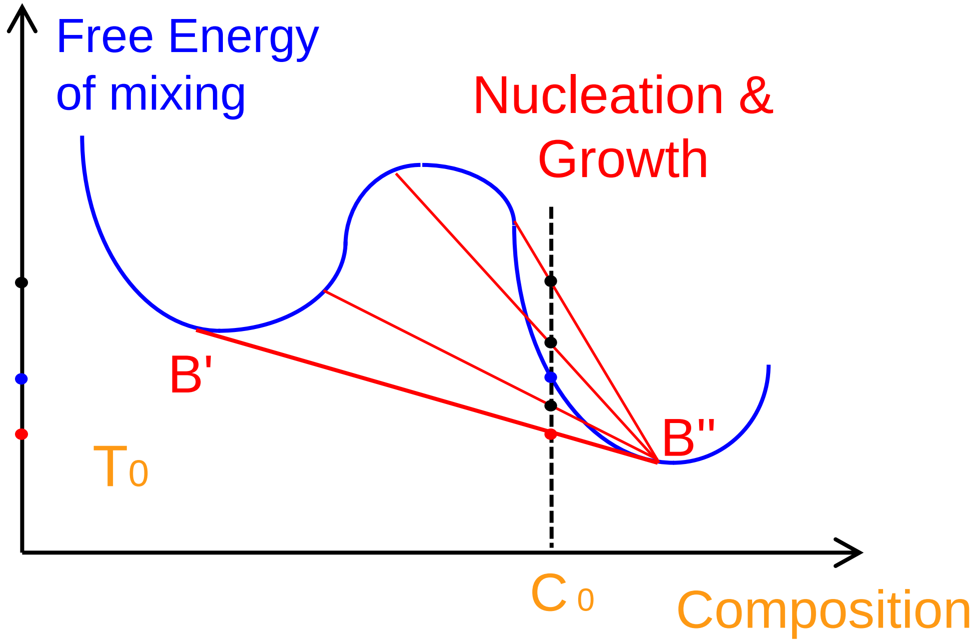


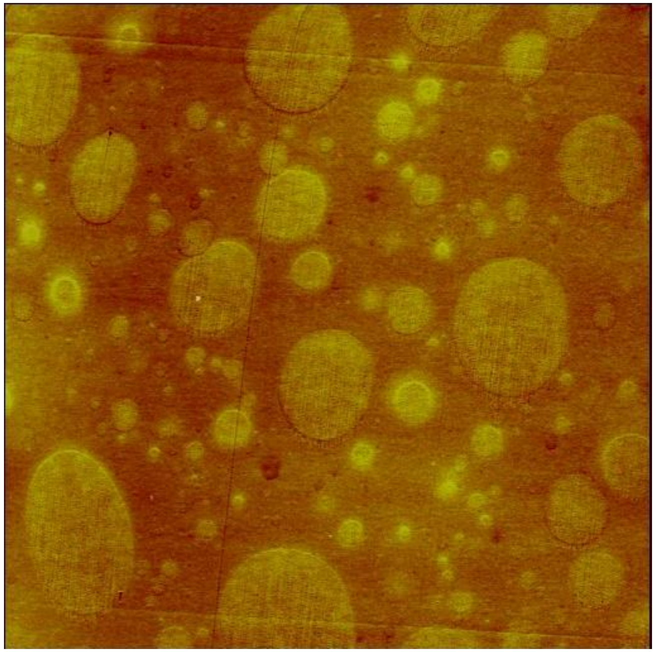
Λ_m: characteristic length of phase separation ~10s-100s nm





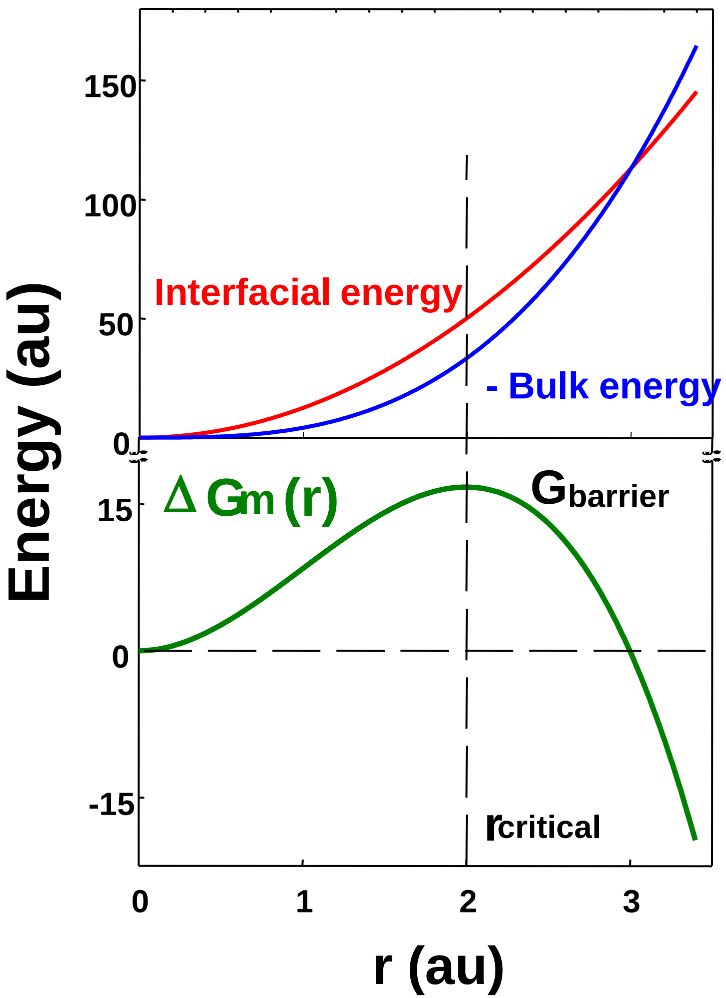
Nucleation & Growth

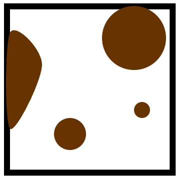




Comparatively SLOW,
since activated process

Nucleation & Growth





Energy balance

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

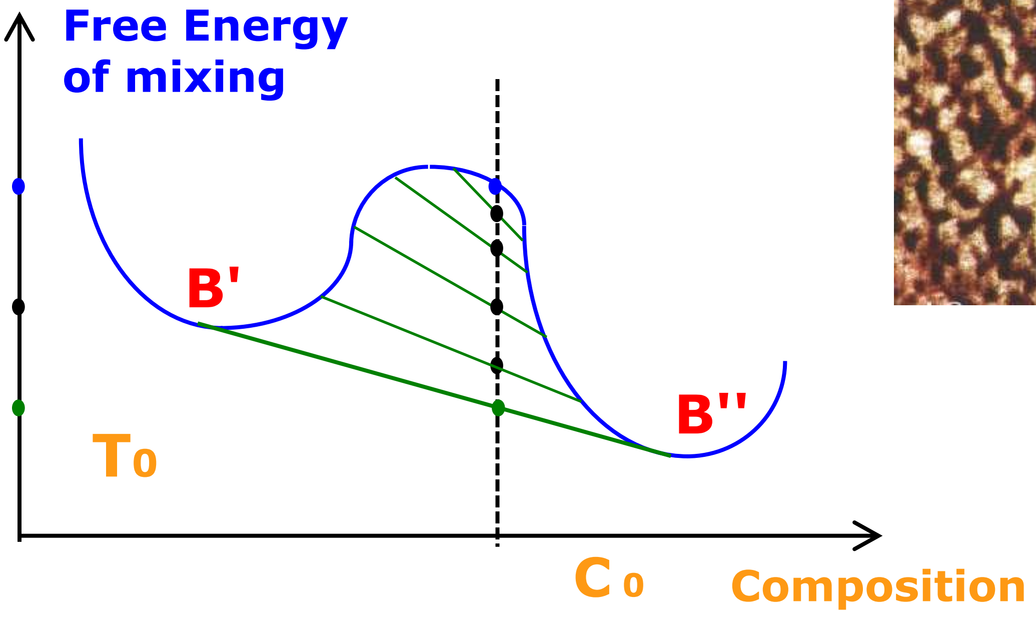
bulk **interface**

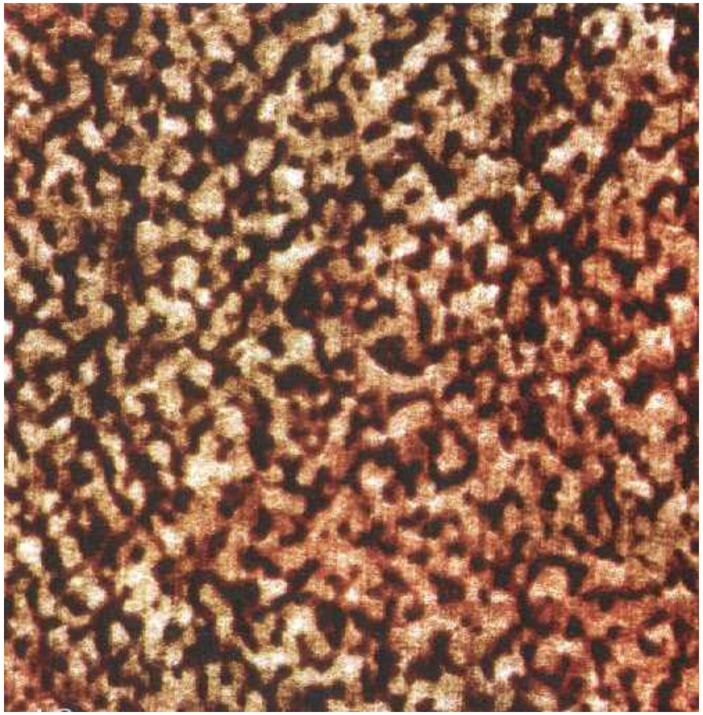
→ **Critical droplet**

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

$r_c = 2\sigma/\Delta g$

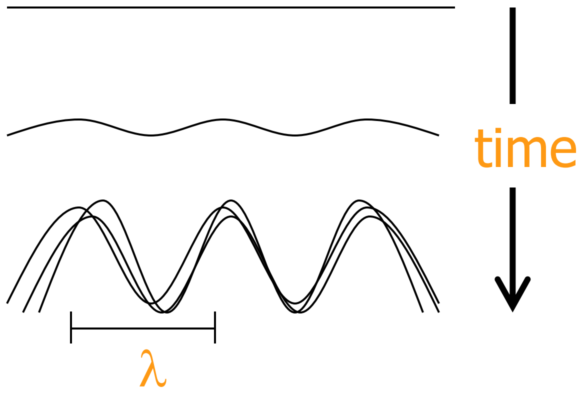
Spinodal decomposition

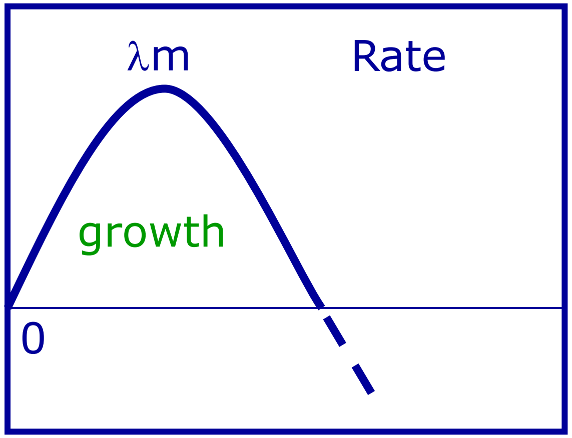




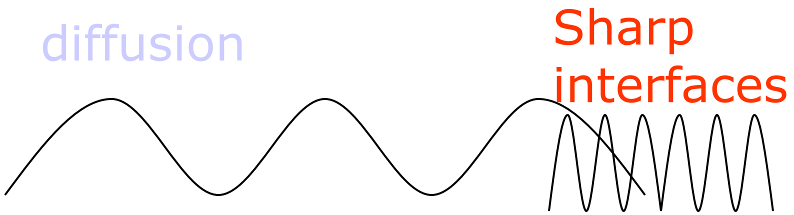
FAST, spontaneous

Spinodal decomposition





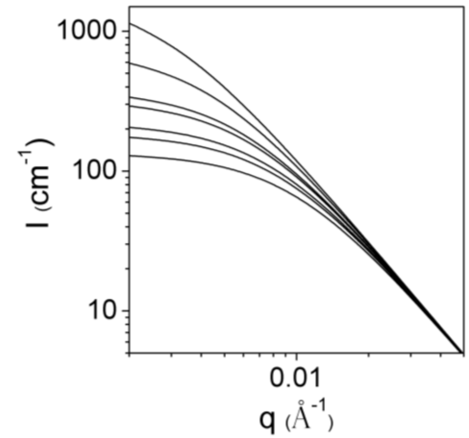
concentration fluctuations



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

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

Cahn-Hilliard Cook theory

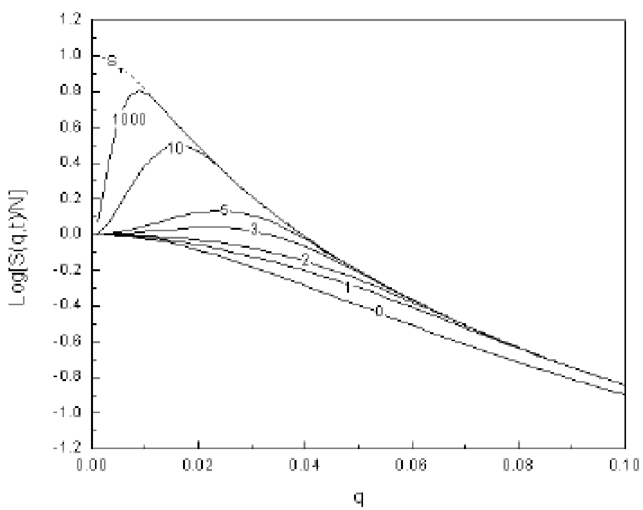


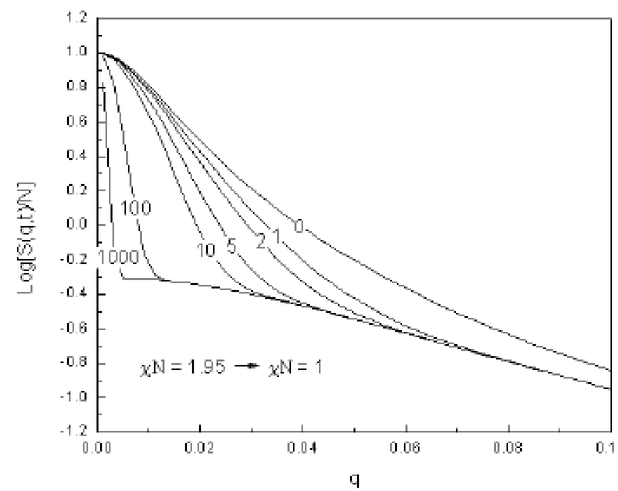
$$S(q,t) = S_T(q) + [S(q,0) - S_T(q)] \exp^{-2\tau_q^{-1} t}$$

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

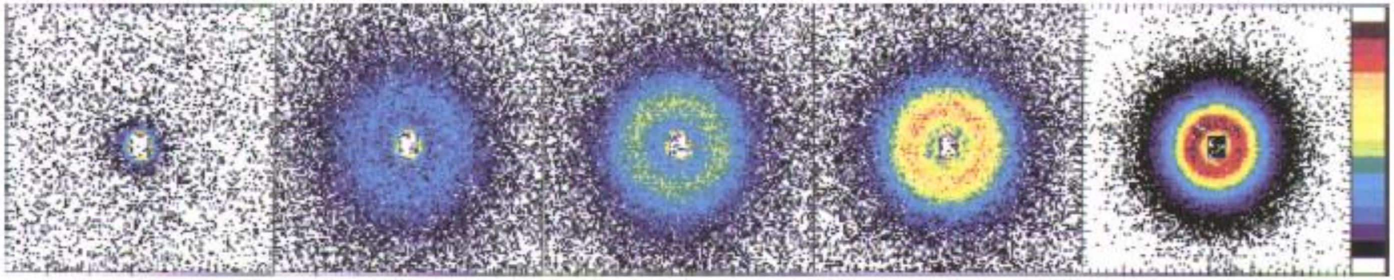
$$\Lambda(q) \quad = \quad W a^2 \phi(1-\phi) g_D(q) \qquad (Rouse\ Model)$$

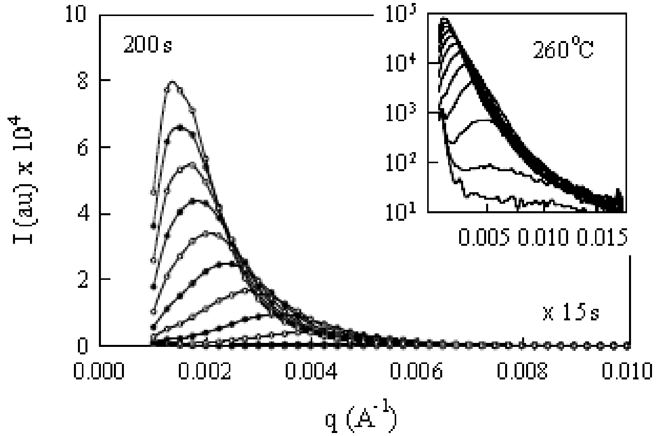
$$\Lambda(q) \quad = \quad \frac{W d^2}{Z} \phi(1-\phi) g_D(q) \qquad (Reptation\ Model)$$



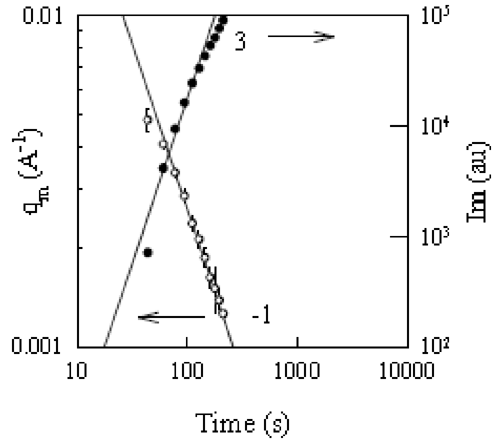


Spatially resolved "rheology"

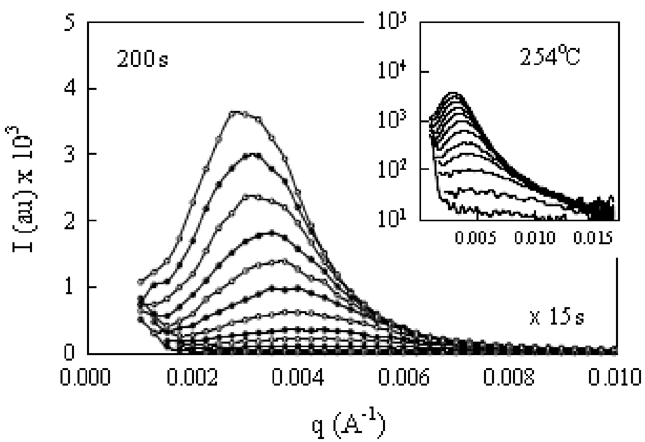




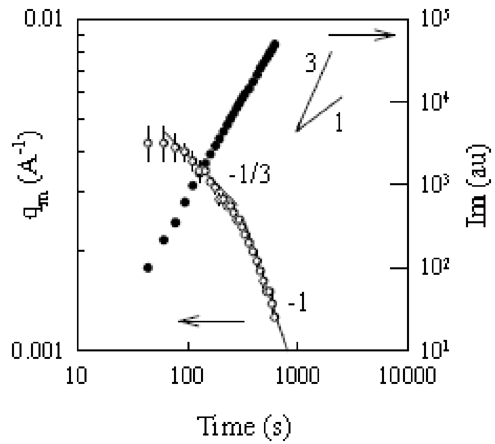
200 s
260°C
x 15 s
I (au) x 10^4
q (A^-1)



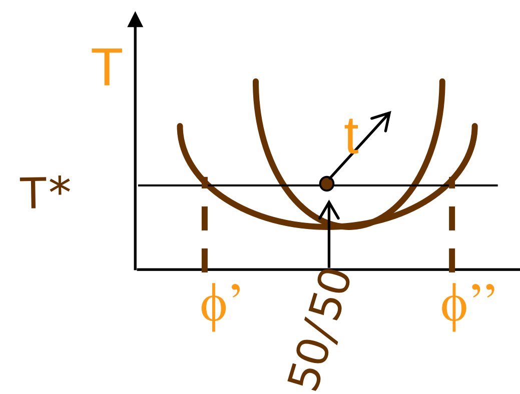
3
-1
q_m (A^-1)
Im (au)
Time (s)



200 s
254°C
x 15 s
I (au) x 10^3
q (A^-1)



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

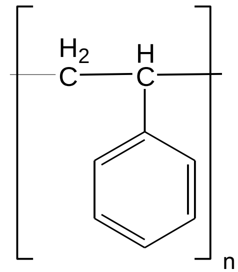


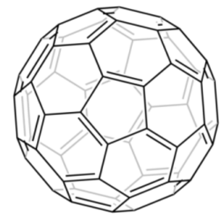
T
T*
t
φ'
50/50
φ''

Opportunities & recent developments

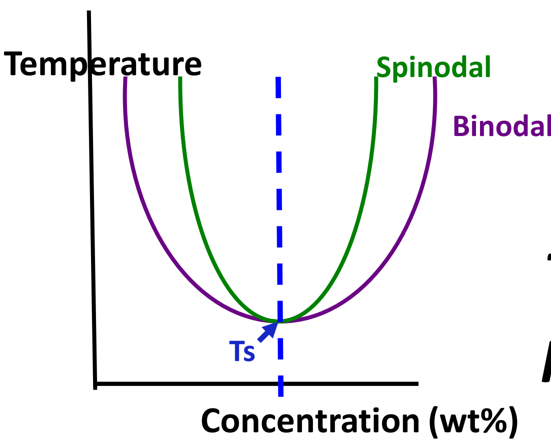
nano*composites*

structure



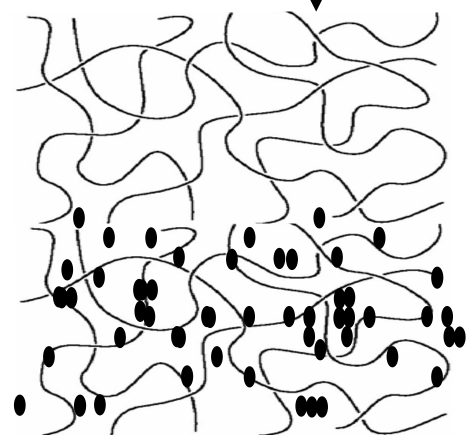


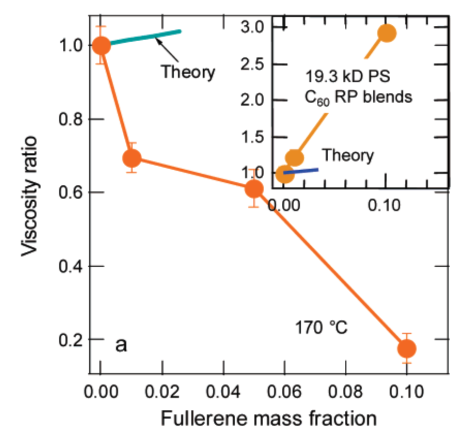
dynamics



Bulk

Thermodynamics & phase separation

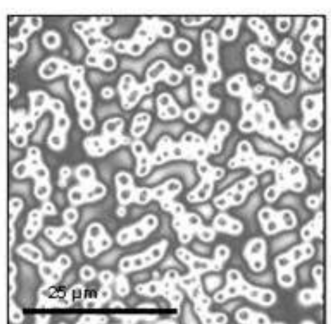




Tuteja et al. Nat. Mat. (2003) 2, 762

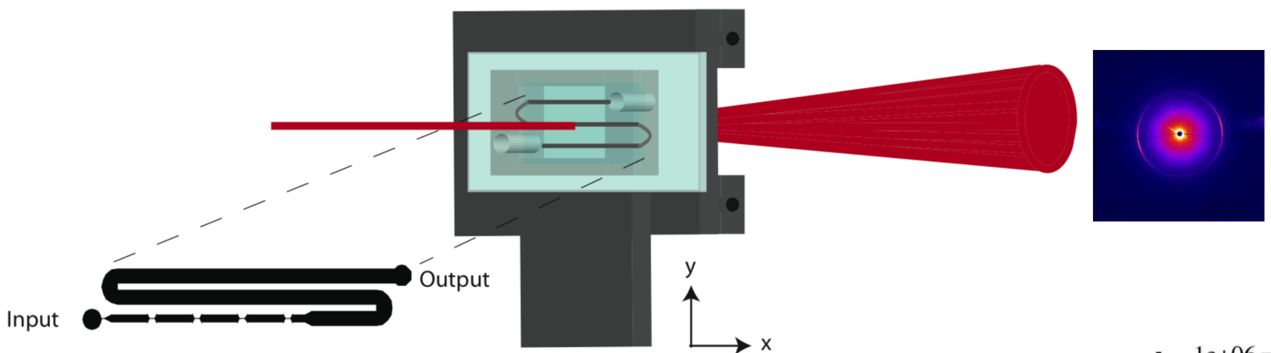
Thin Films

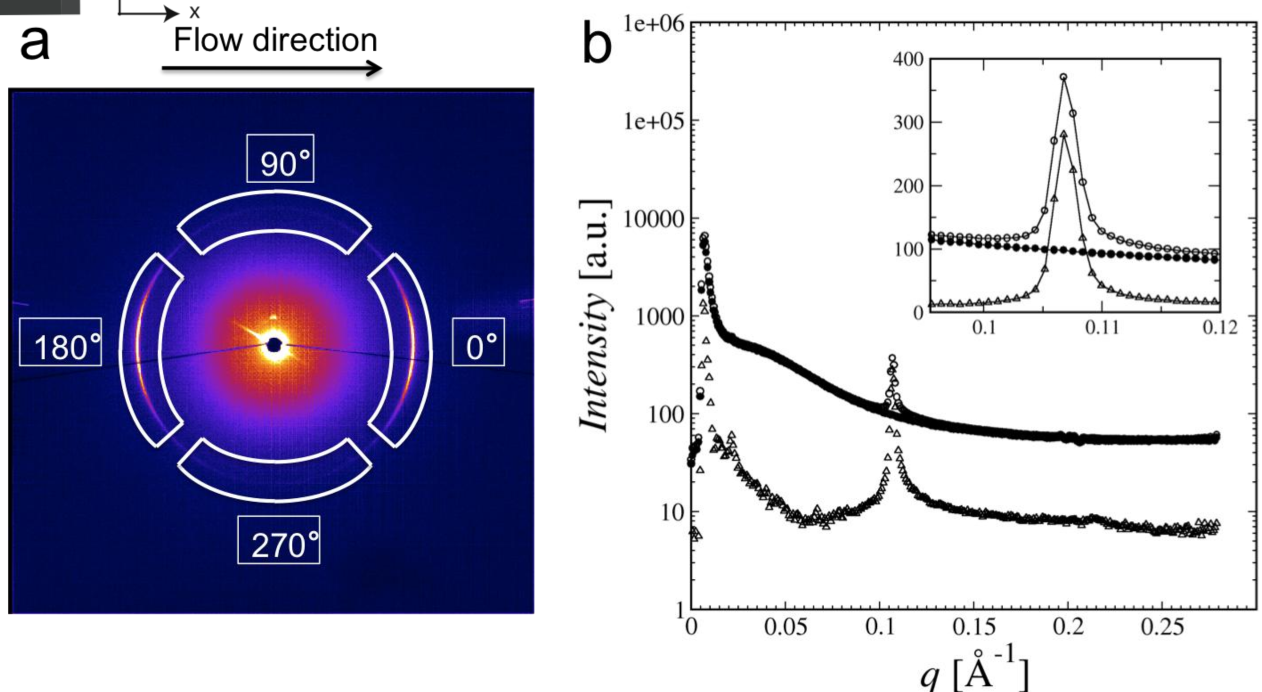
Morphology



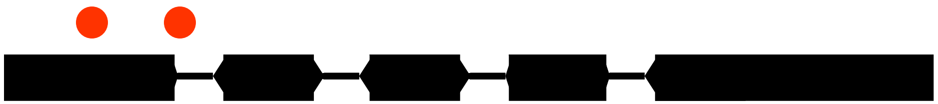
Flow fields (and microfluidics?)

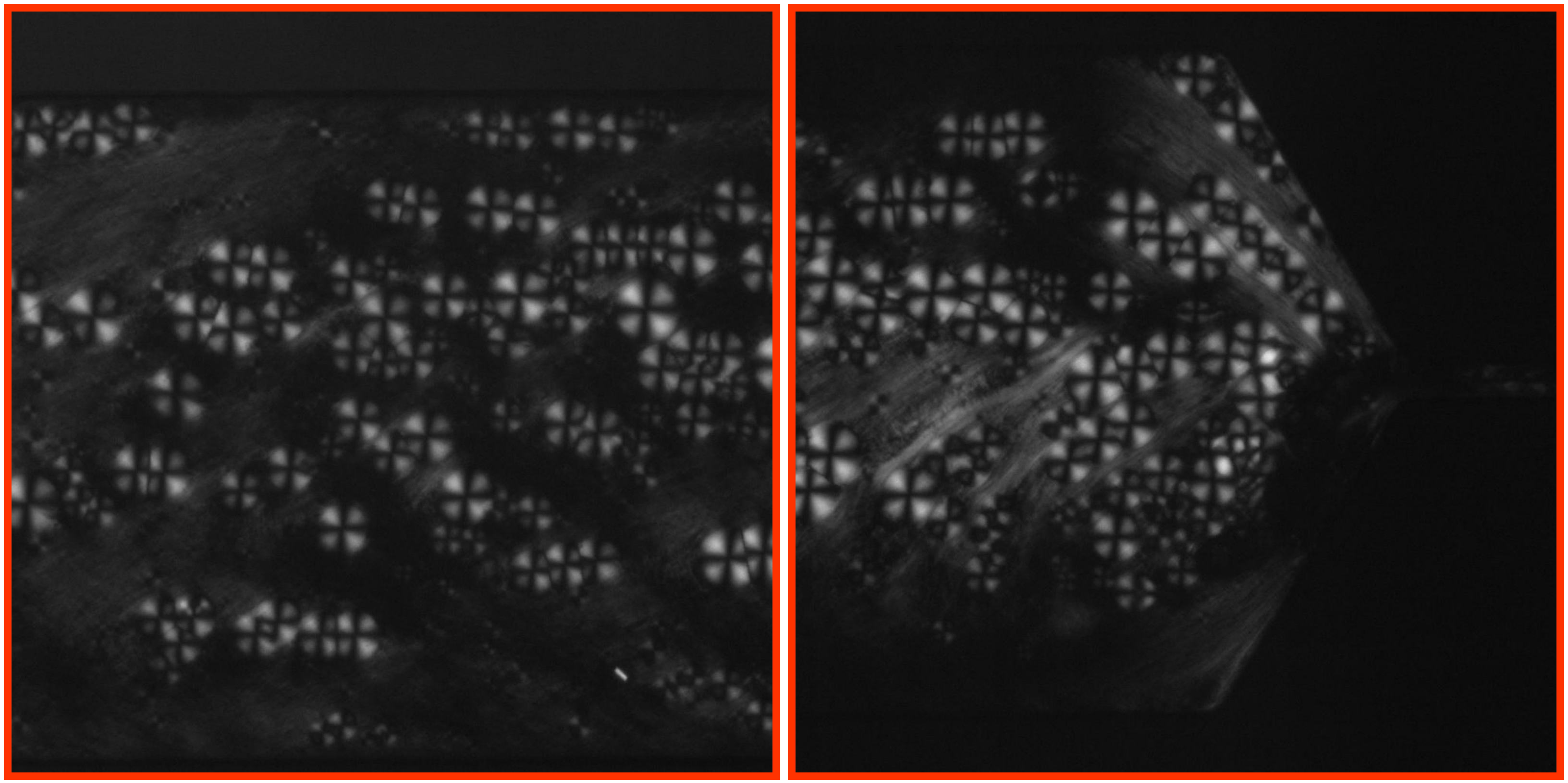
CTAC/ Pentanol/Water



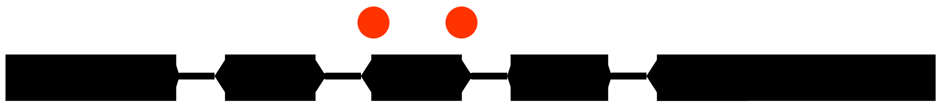


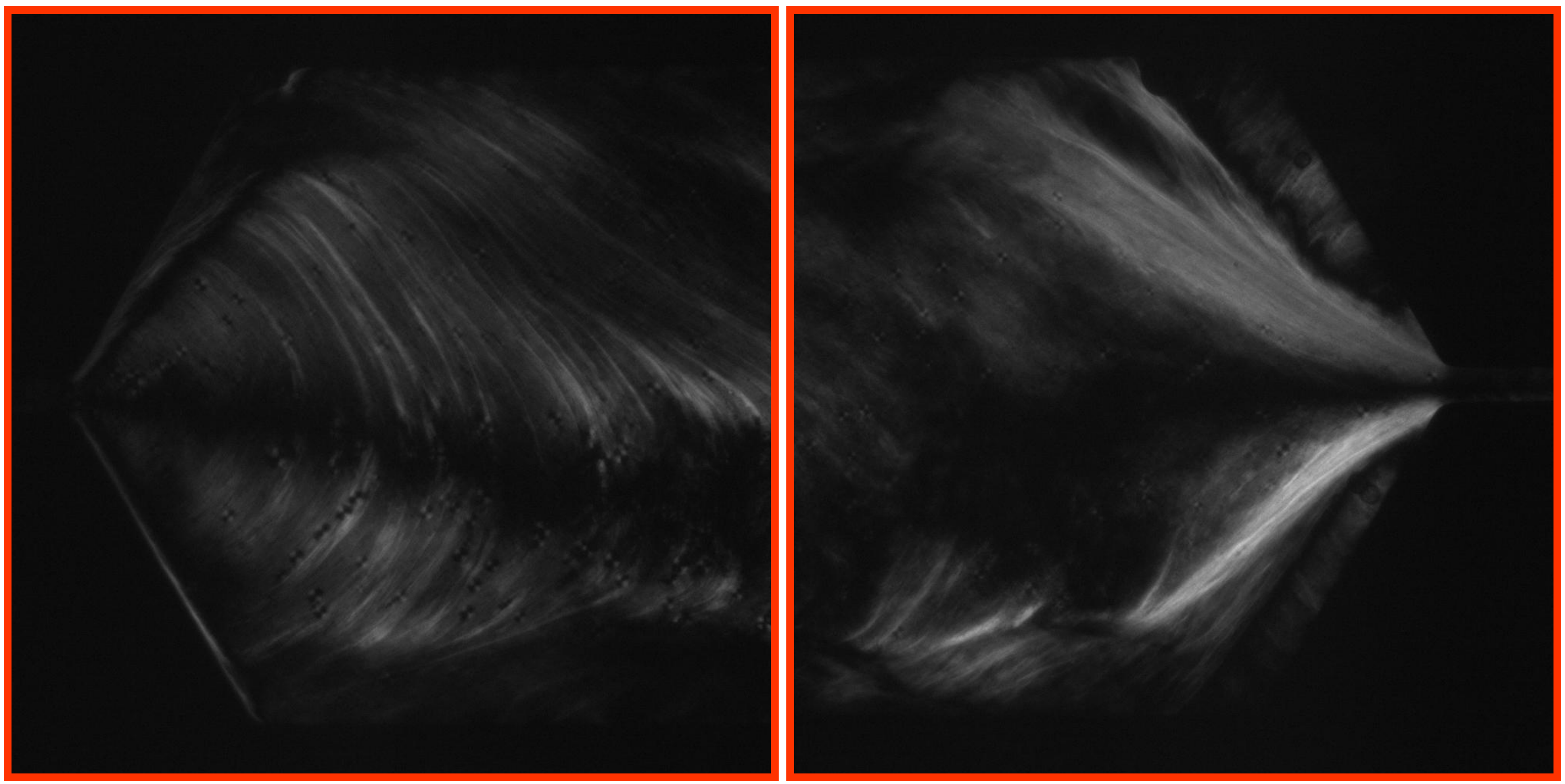
Periodic constrictions: contraction/expansion flows



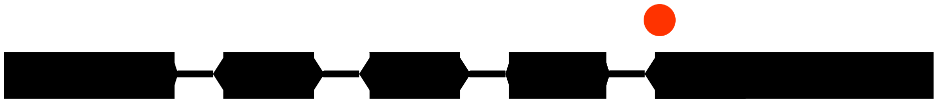


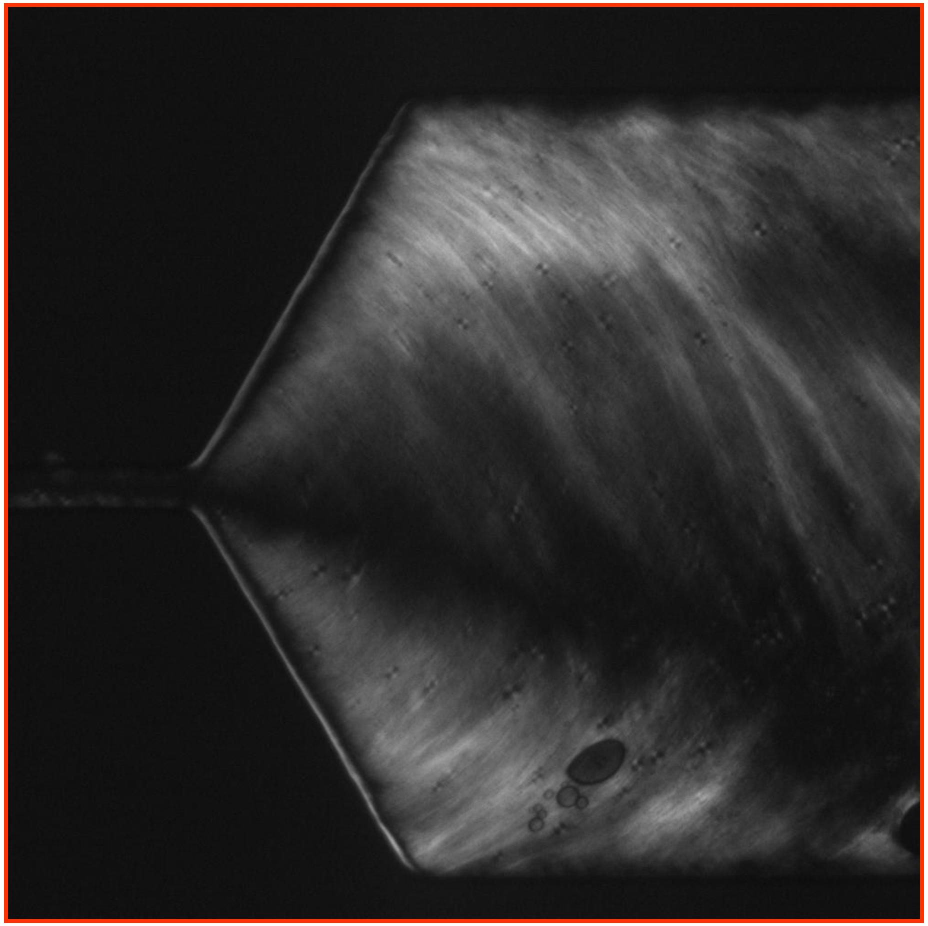
Periodic constrictions: contraction/expansion flows



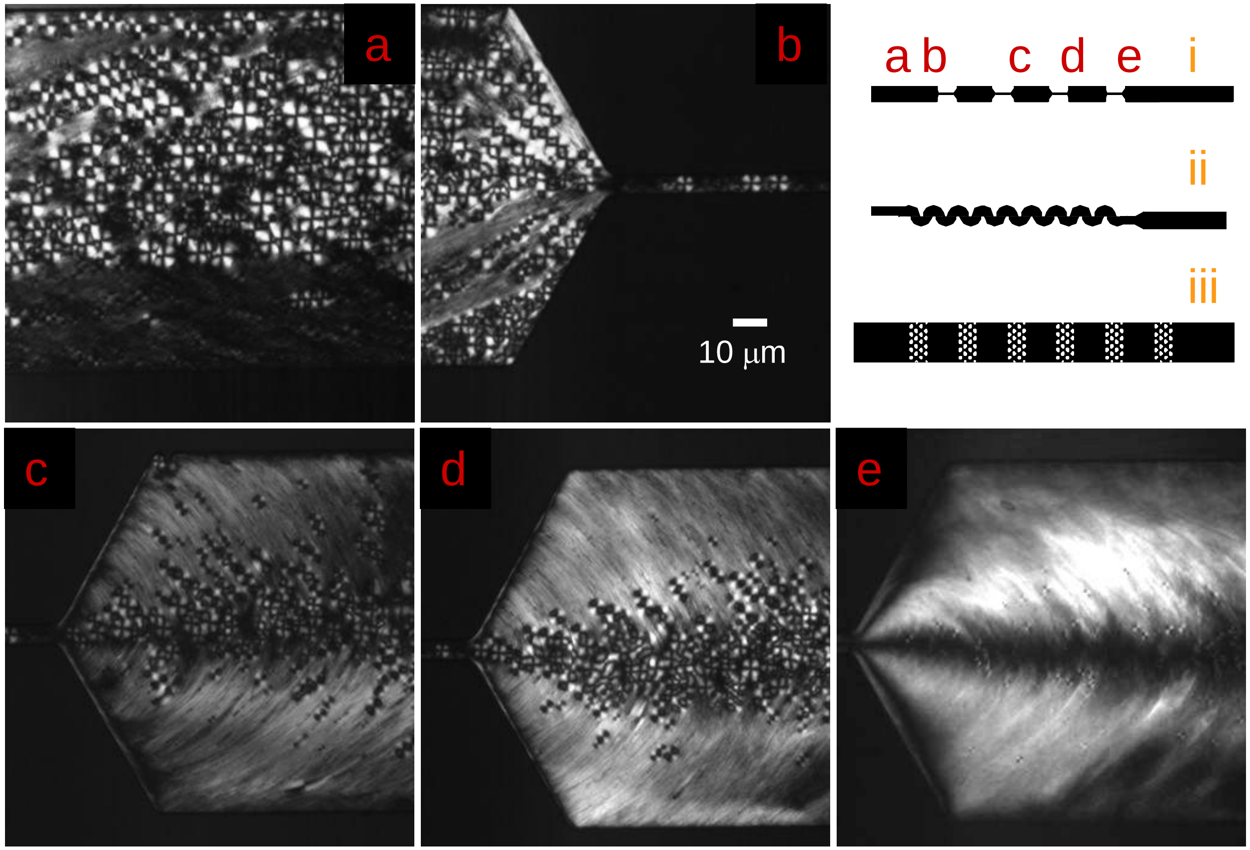


Periodic constrictions: contraction/expansion flows



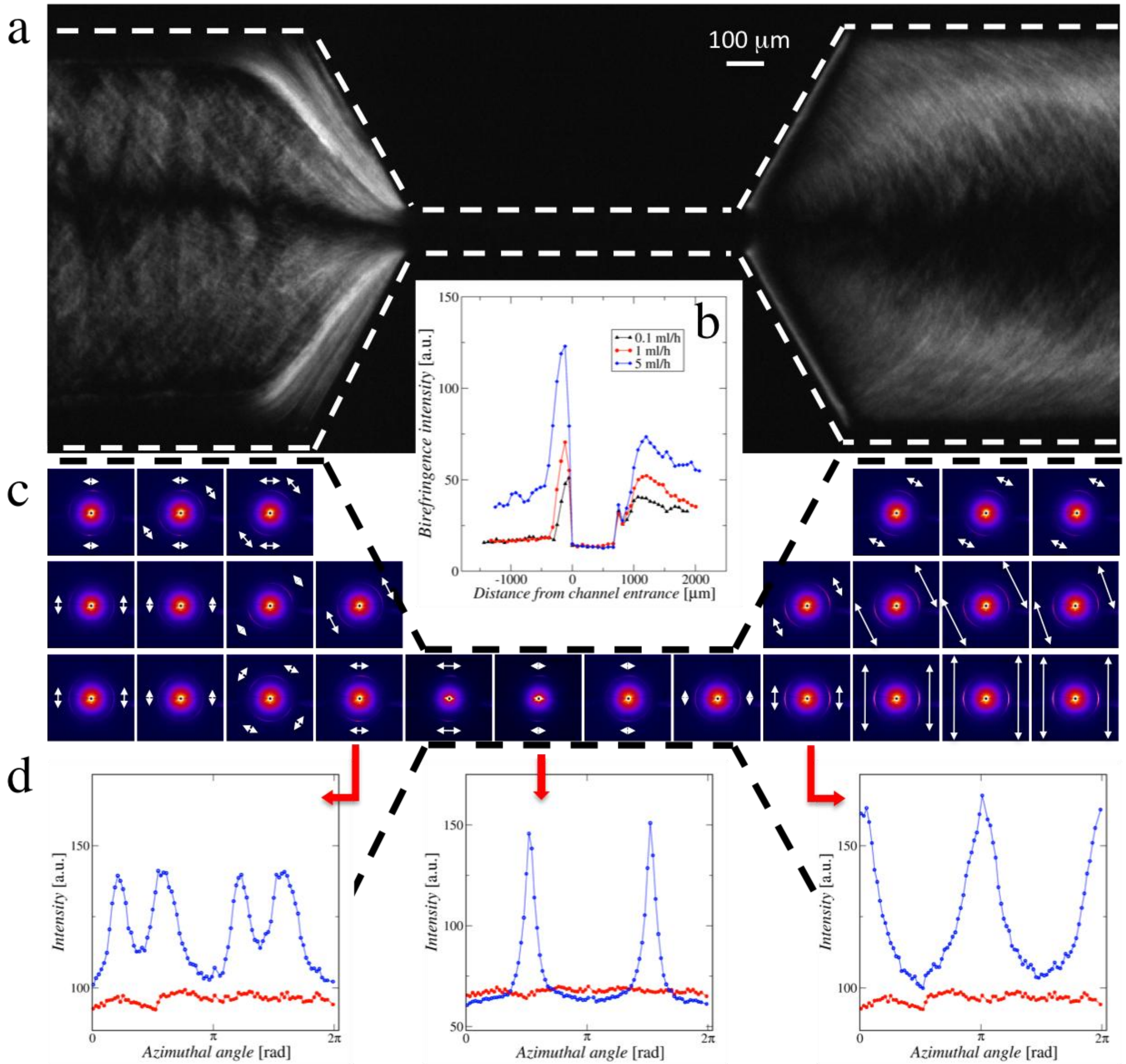


Periodic constrictions: contraction/expansion flows



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

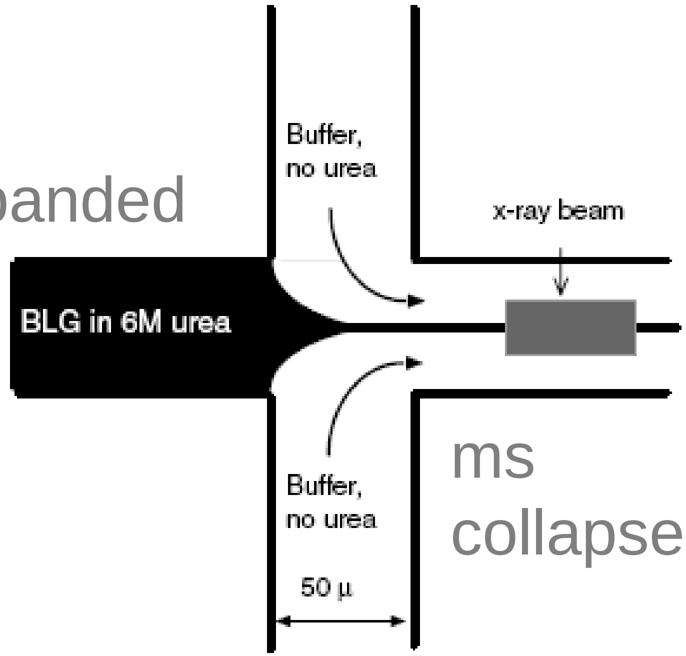
Conclusion: *Microstructure alignment & orientation*



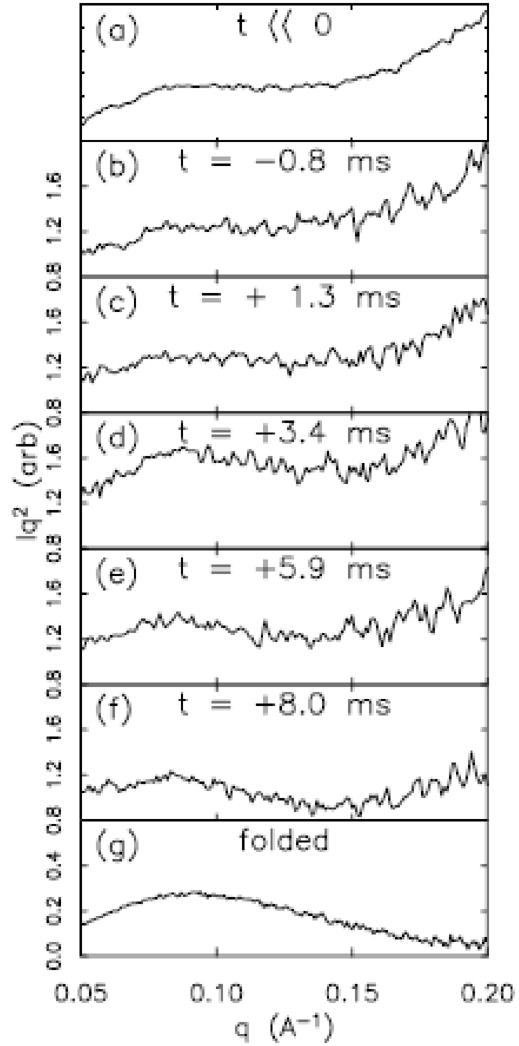
Spatio-temporal mapping:

Coil-to-globule transition

expanded



ms
collapse

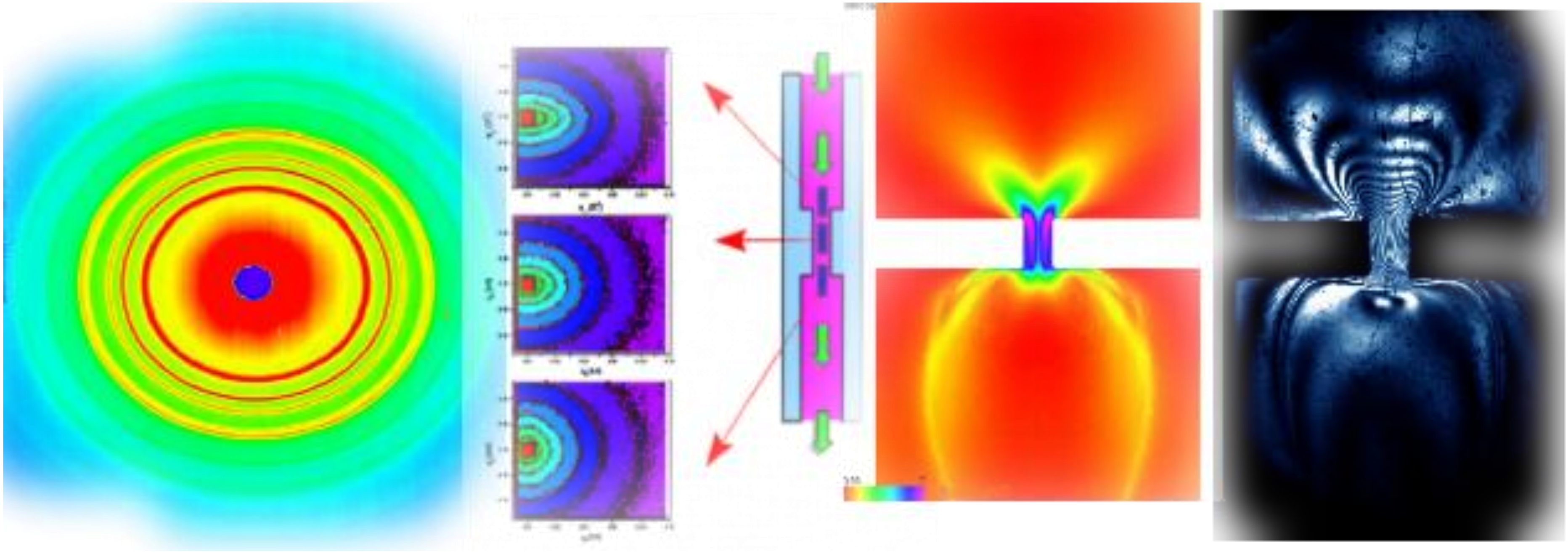


β-lactoglobulin (BLG)

(Pollack, Austin, etc)

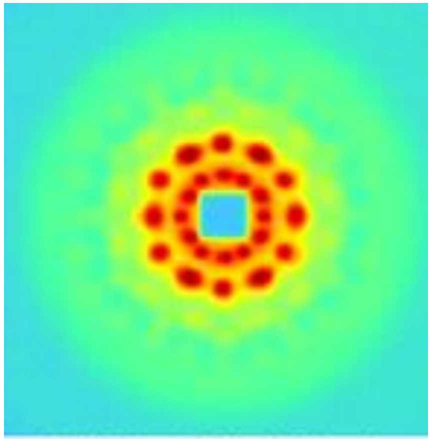
Spatio-temporal mapping:

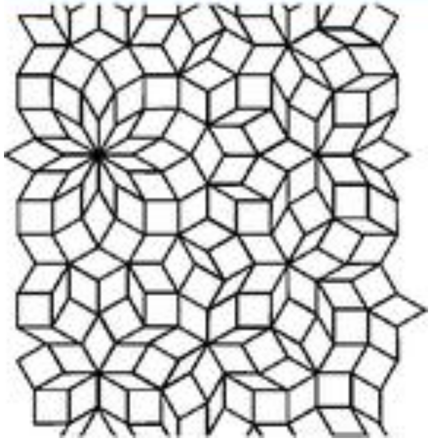
Entangled polymers under flow

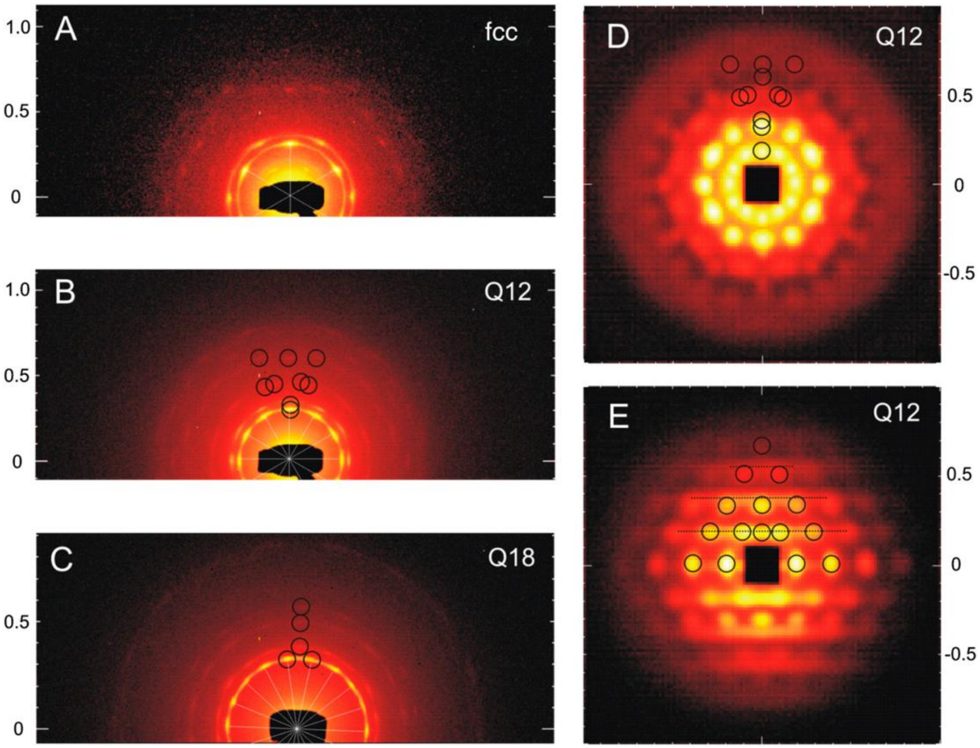


Neutron-Mapping Polymer Flow: Scattering, Flow Visualization, and Molecular Theory
J. Bent, *et al.*
Science 301, 1691 (2003);

Soft colloids under flow

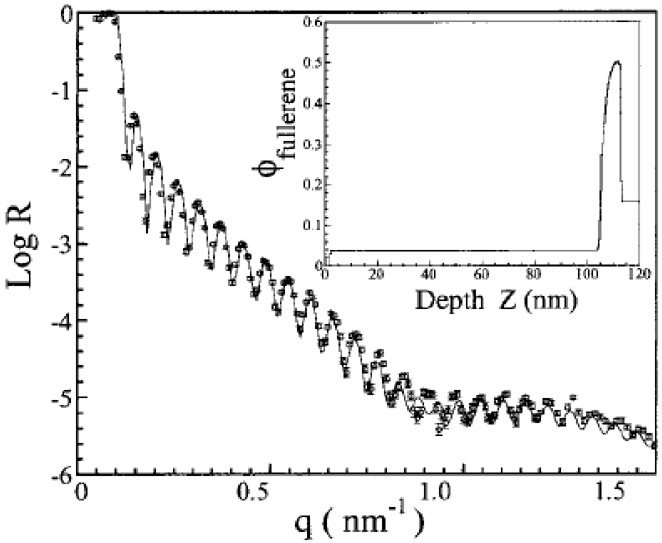




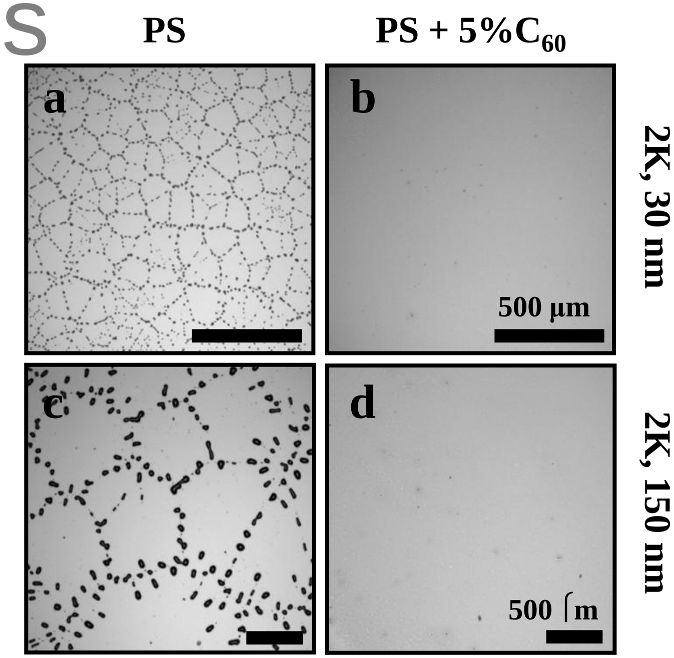


Forster et al. PNAS 2011

Design 3D composites

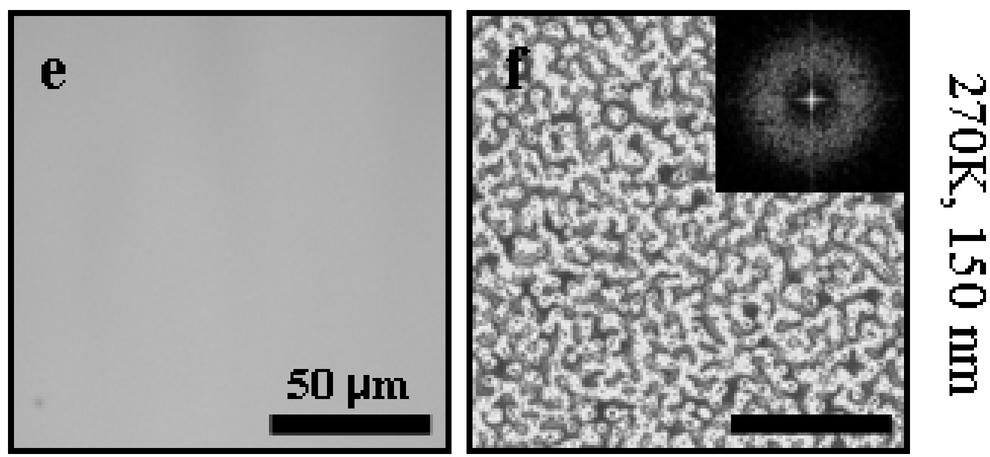


PS+5% C60 h = 100nm



140ºC

180ºC



180ºC

GISANS & reflecometry

PRL 2010

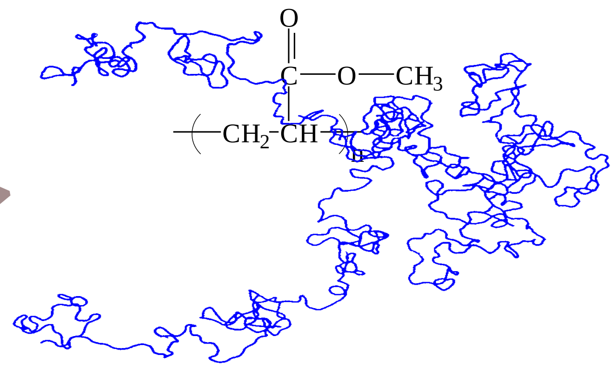
'Spinodal Clustering'

Summary

① Intro

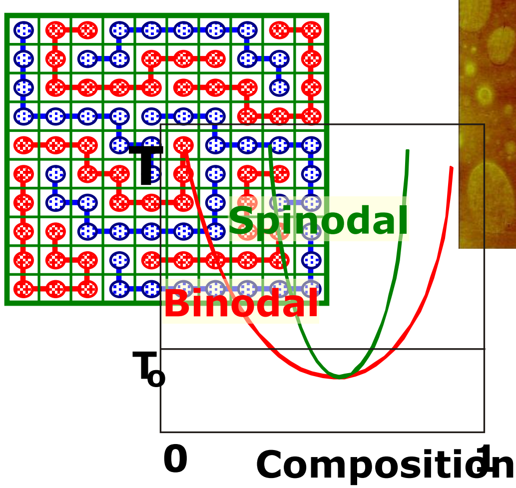
History

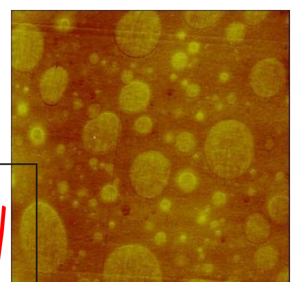
② Soft matter



③ Form and structure

④ Mixtures & design





⑤ Outlook