Imperial College London

Neutrons in soft matter

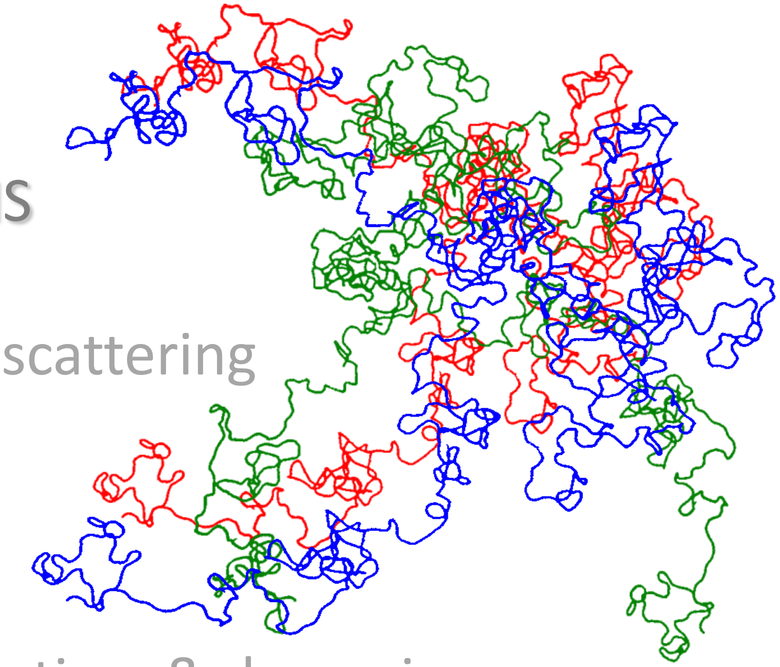
Lecture 2 – Reflectometry & Dynamics

João T. Cabral & Julia S Higgins
Department of Chemical Engineering
Imperial College London

David G Bucknall
Georgia Tech, USA

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...

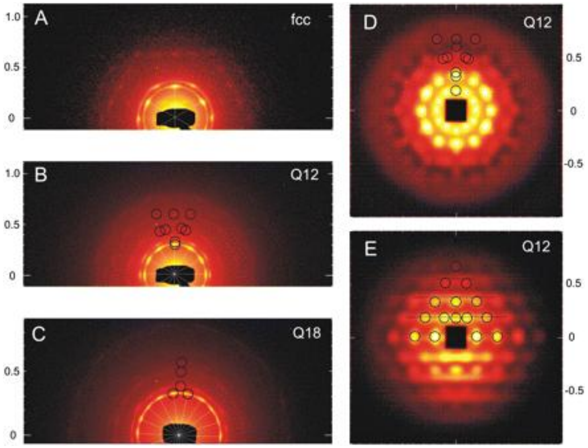
Single chain polymer conformation
(solution and blends)

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

Lecture 2 – Interfaces and dynamics

Reflectivity and diffusion

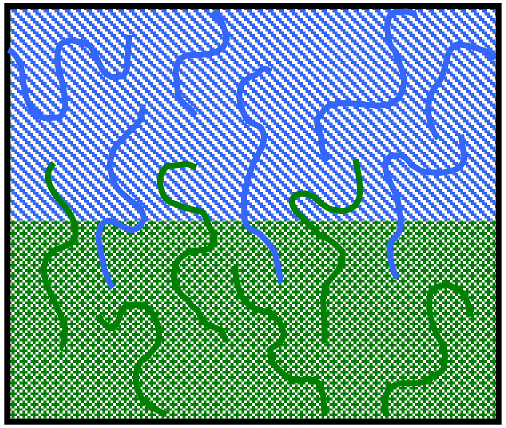
Dynamics in soft matter, QENS, BS, Spin-echo



Forster et al (2011)

Reflectometry: study of interfaces

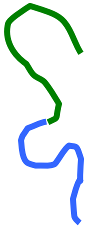
Miscible systems



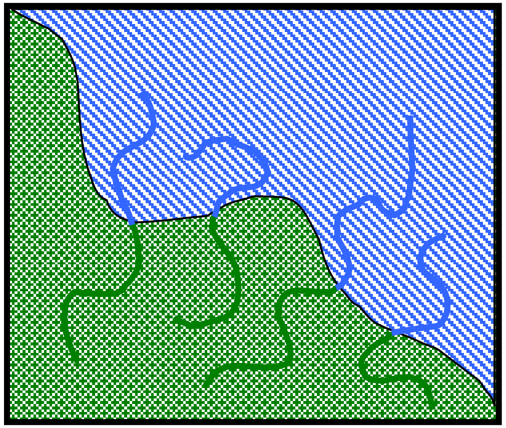
- Interdiffusion, e.g., welding

Immiscible systems

- Copolymers, e.g., di-blocks

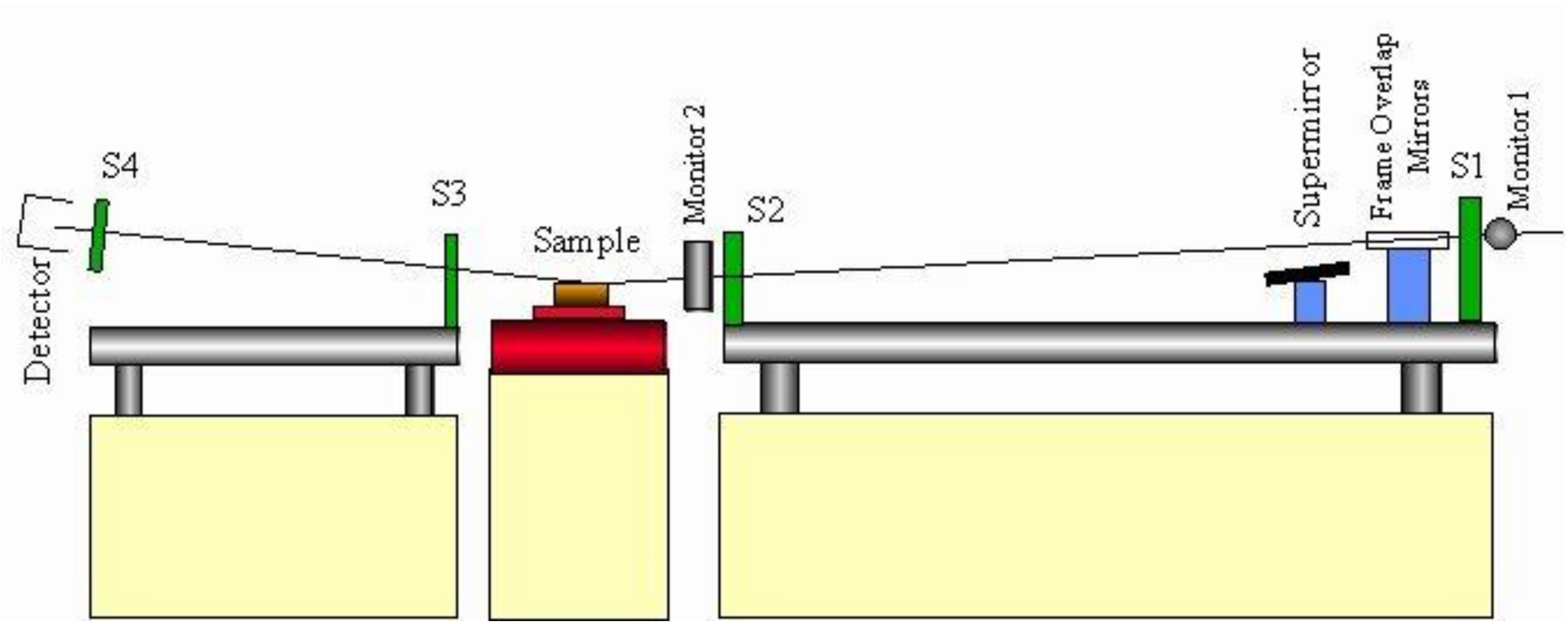


- Reduce interfacial tension
→ smaller dispersed phase



- Entangle with homopolymers
→ increase strength

Reflectometry



CRISP (ISIS)

Significance of the interfacial width

Theoretical width

- Infinite molecular weight limit

$$w_t = \frac{2a}{(6\chi)^{0.5}}$$

E Helfand & AM Sapse
J Chem Phys 62 (1975) 1327

where a (statistical segment length)

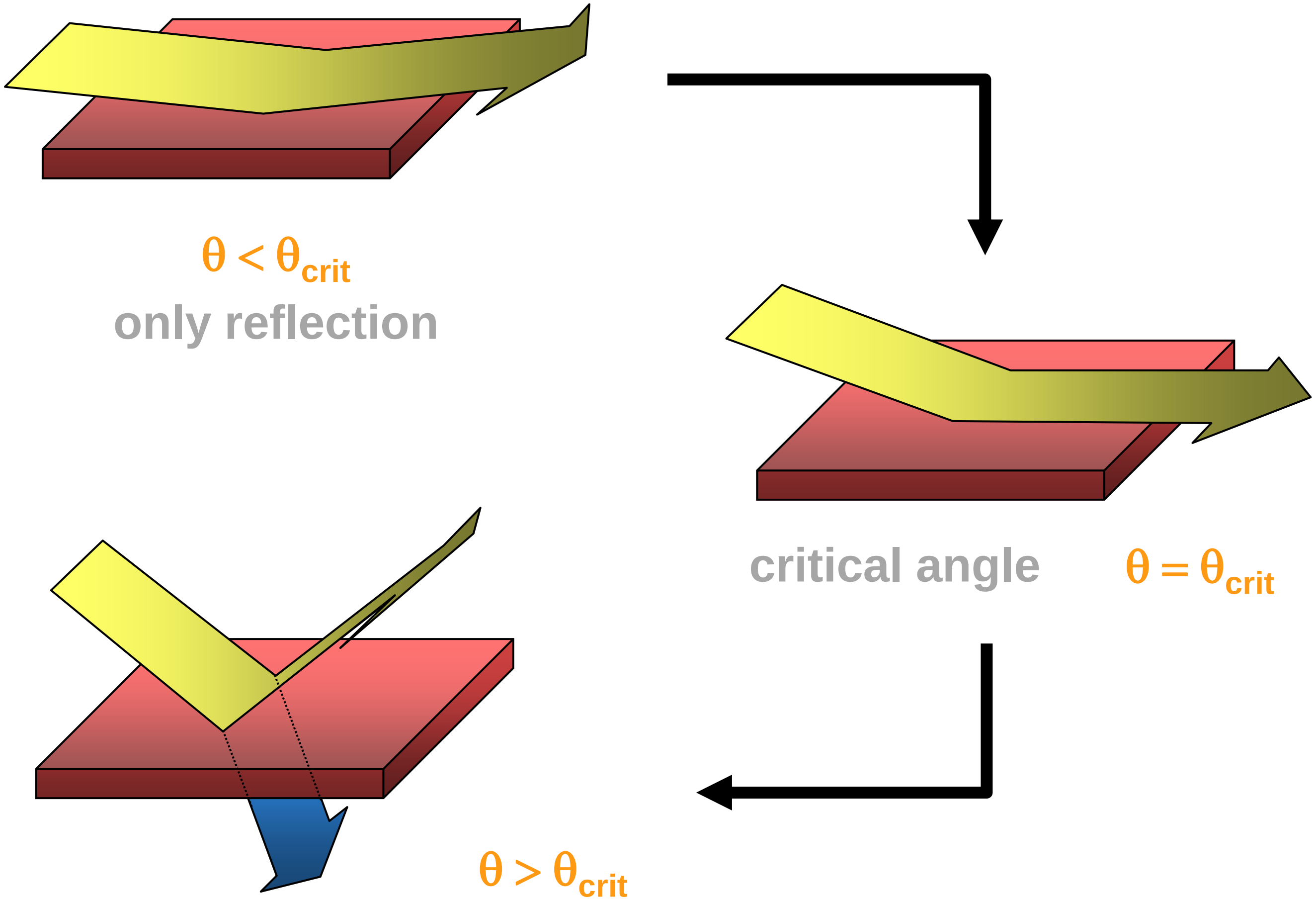
- Finite molecular weight limit

$$w_t = \frac{2a}{\sqrt{6}}\left(\chi - \frac{\pi^2}{6}\left(N_1^{-1} + N_2^{-1}\right)\right)^{-1/2}$$

M Stamm & DW Schubert
Ann Rev Mater Sci
25 (1995) 325

$\Rightarrow$ Measure interfacial width to find χ

Basics of Reflectivity



$\theta < \theta_{crit}$

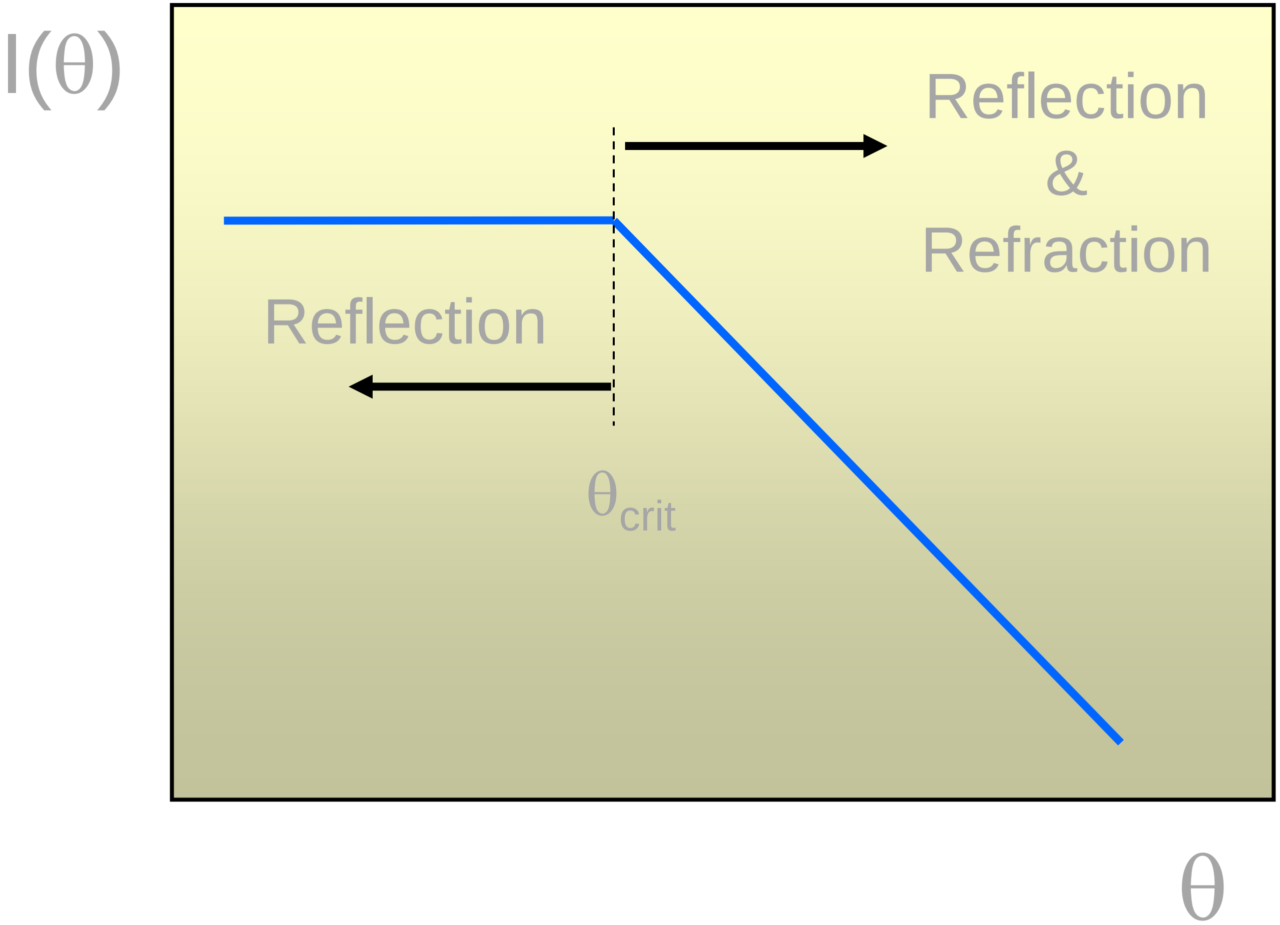
only reflection

critical angle $\theta = \theta_{crit}$

$\theta > \theta_{crit}$

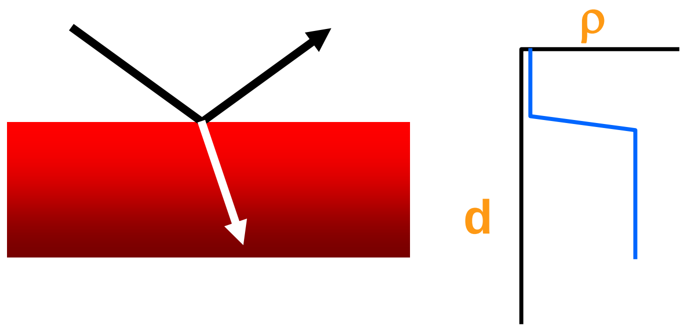
reflection and refraction

The Reflectivity Profile



Information Content

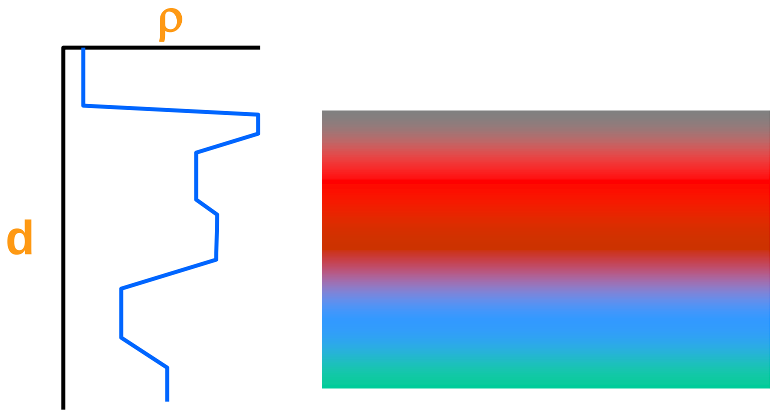
Simplest Case



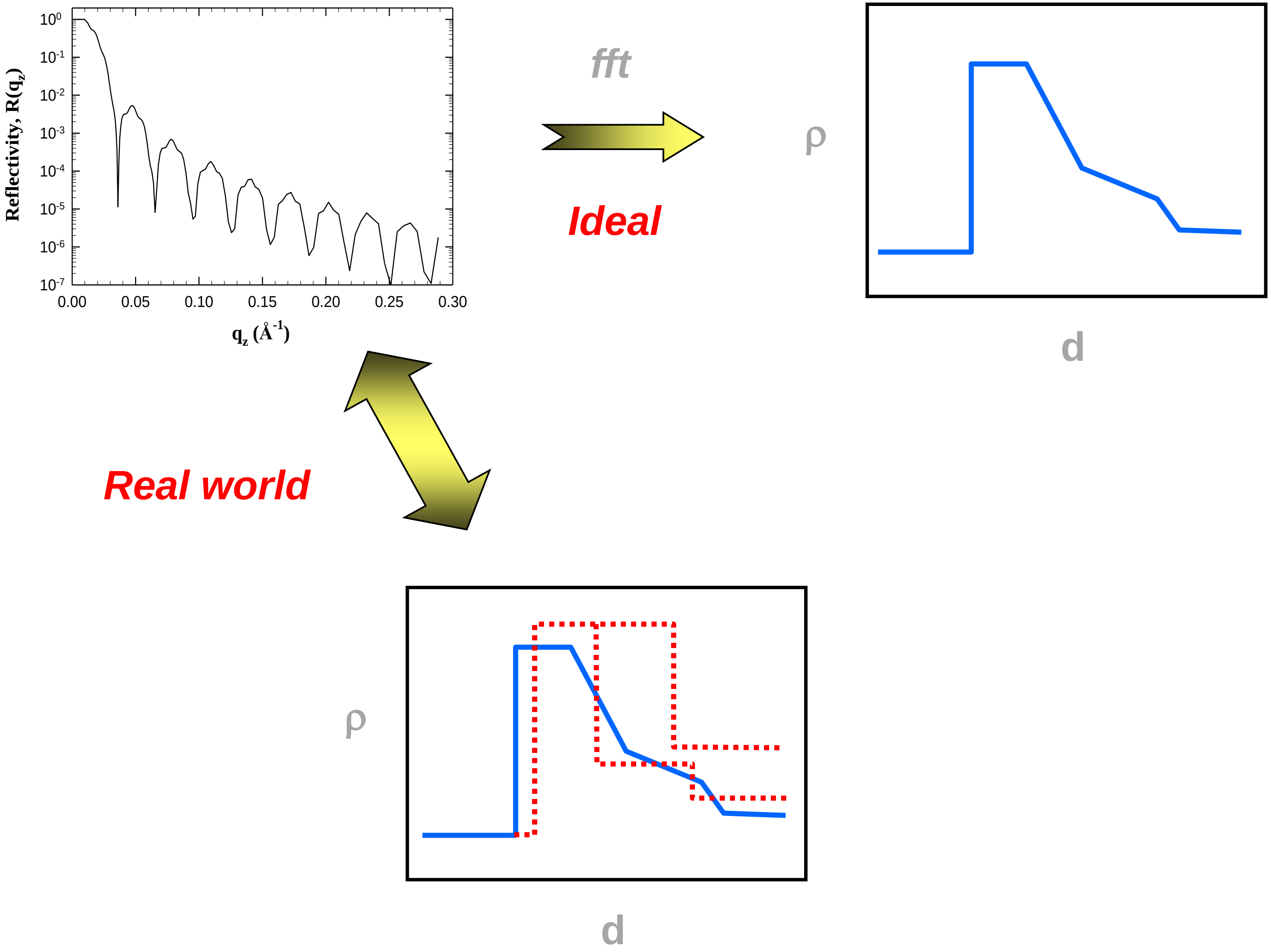
What about lateral information?

Off-specular !

Complex Case



Evaluating Reflectivity Data

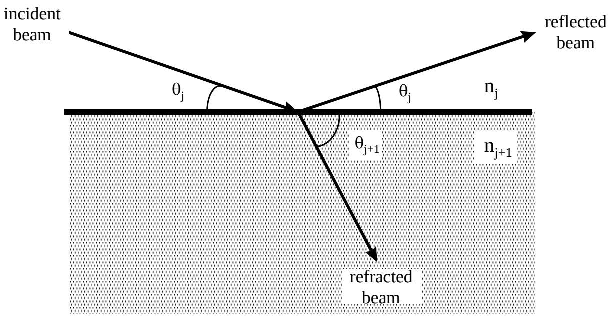


fft

Ideal

Real world

Single layers and bilayers



$$n_j = 1 - \frac{\lambda^2 N_d b}{2\pi} = 1 - \frac{\lambda^2 \rho_z}{2\pi}$$

$$n_j \cos\theta_j = n_{j+1} \cos\theta_{j+1}$$

Snell's Law

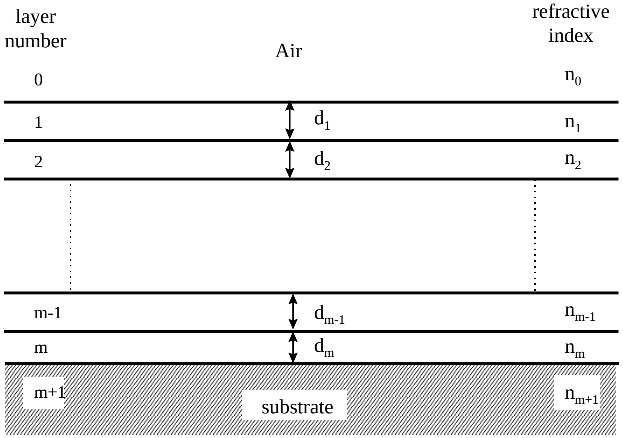
$$r_{j,j+1} = \frac{n_j \sin\theta - n_{j+1} \sin\theta_{j+1}}{n_j \sin\theta + n_{j+1} \sin\theta_{j+1}}$$

Fresnel's law

$$q = 2k = \frac{4\pi}{\lambda} \sin\theta$$

$$r_{j,j+1} = \left(\frac{q_{z,j} - q_{z,j+1}}{q_{z,j} + q_{z,j+1}} \right)$$

$$R = r_{j,j+1} r^{*}_{j,j+1}$$



$$r'_{m-1,m} = \frac{r_{m-1,m} - r_{m,m+1} \exp(2i\beta_m)}{1 + r_{m-1,m} r_{m,m+1} \exp(2i\beta_m)}$$

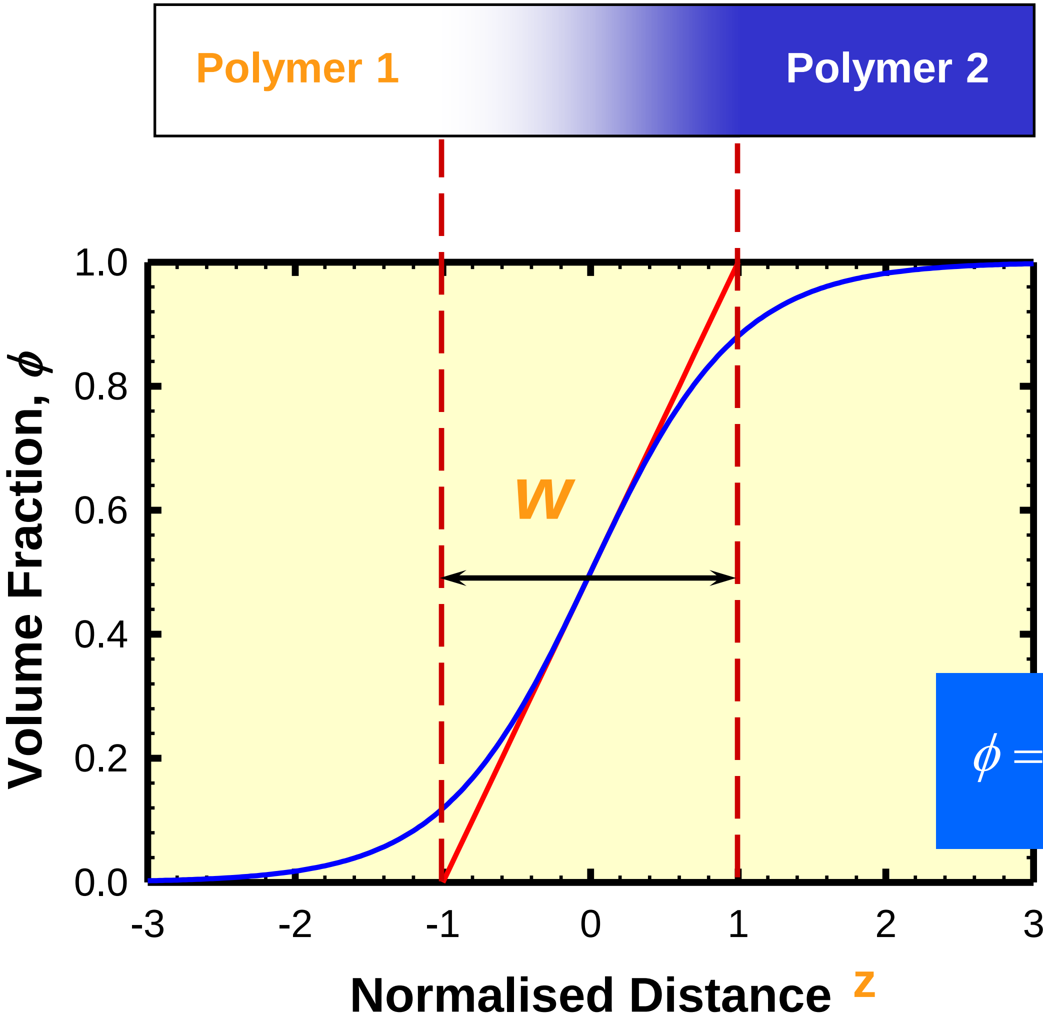
$$\beta_m = (2\pi/\lambda) n_m d_m \sin\theta$$

$$c_m = \begin{bmatrix} \cos\beta_m & -(i/\kappa_m)\sin\beta_m \\ -i\kappa_m \sin\beta_m & \cos\beta_m \end{bmatrix}$$

$$M = \prod_{m=0}^{m} c_m = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix}$$

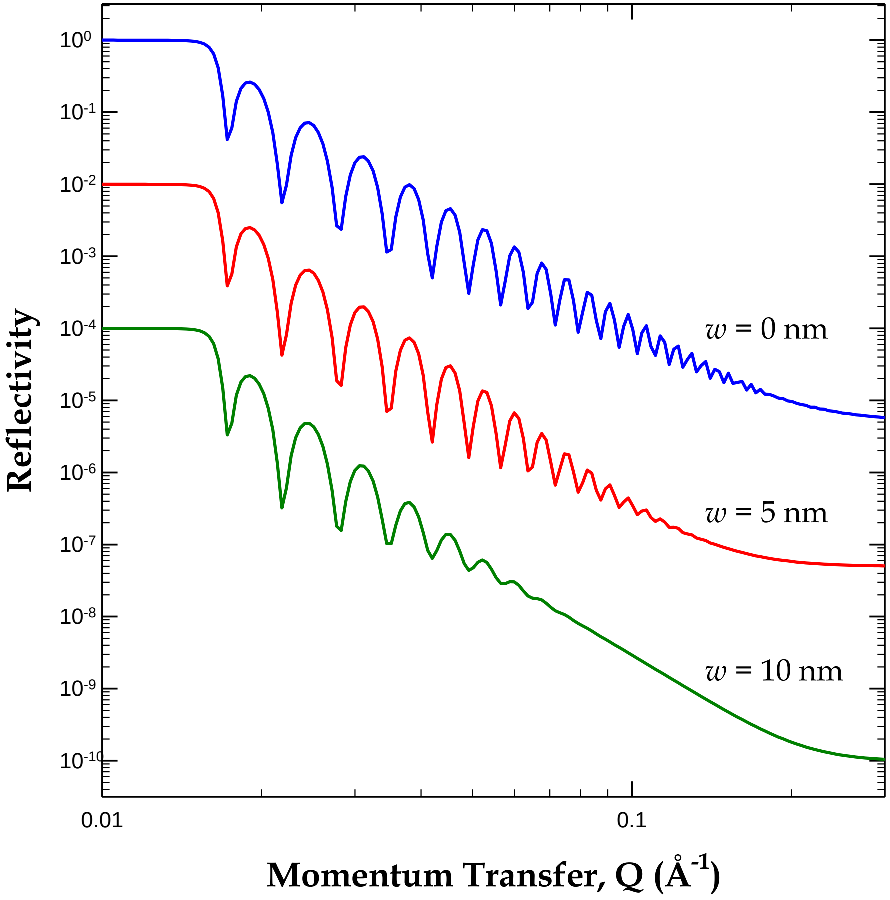
$$R = \left| \frac{(M_{11} + M_{12}\kappa_{m+1})\kappa_0 - (M_{21} + M_{22})\kappa_{m+1}}{(M_{11} + M_{12}\kappa_{m+1})\kappa_0 + (M_{21} + M_{22})\kappa_{m+1}} \right|^2$$

Interfacial Width - Definition

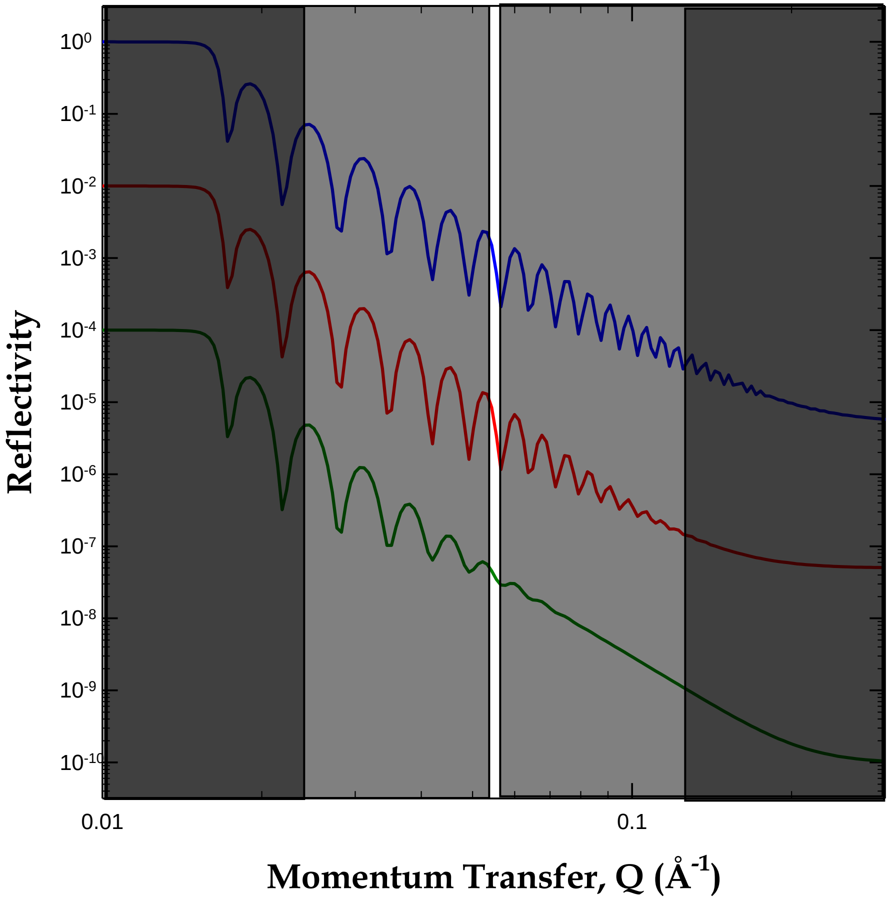


$$\phi = \frac{1}{2}\left(1 + \tanh\left(\frac{2\boldsymbol{z}}{\boldsymbol{w}}\right)\right)$$

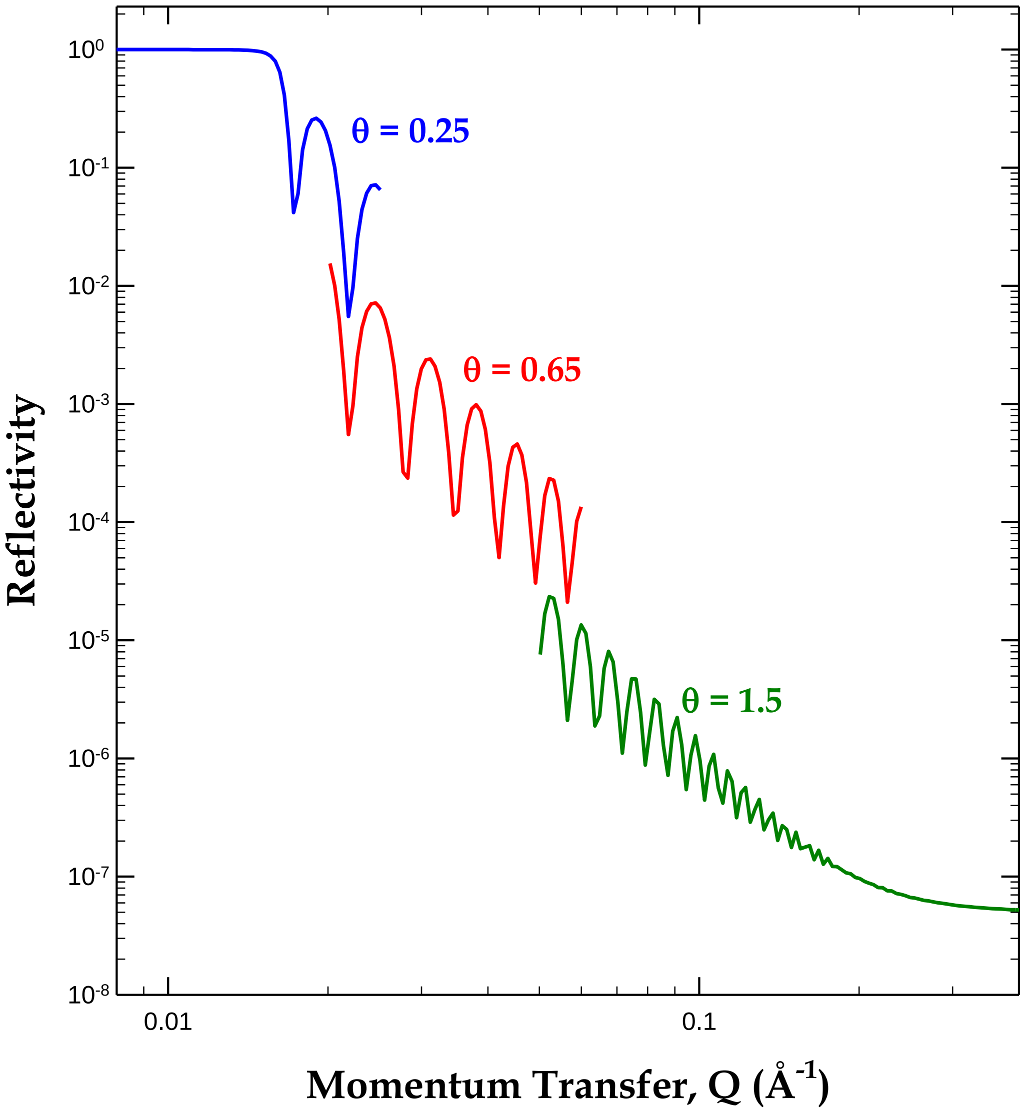
Effect of Interdiffusion on Reflectivity Profiles

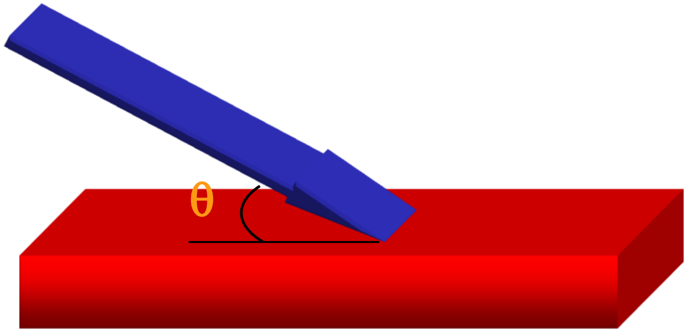


Effect of Limiting
Q range on Observation Window



Effect of Angle on the Q Range

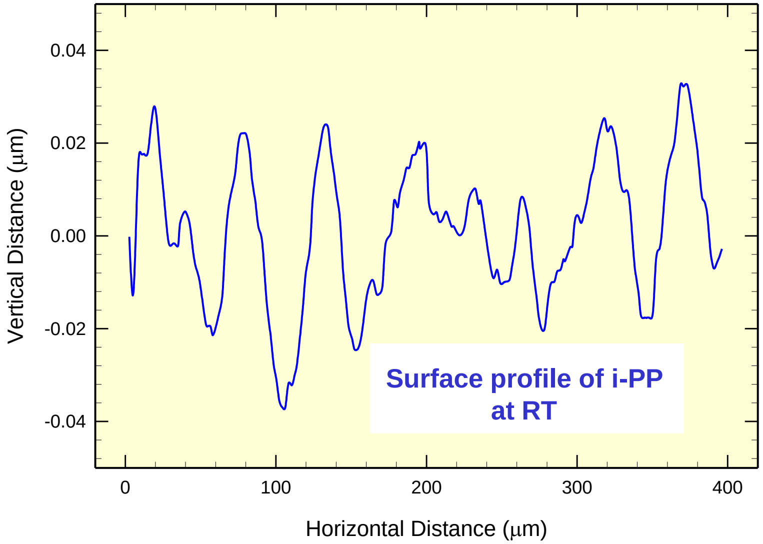




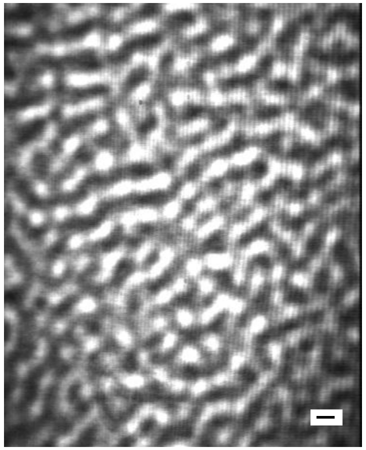
$$Q = \frac{4\pi}{\lambda}\sin\theta$$

0.05 < λ (nm) < 0.65

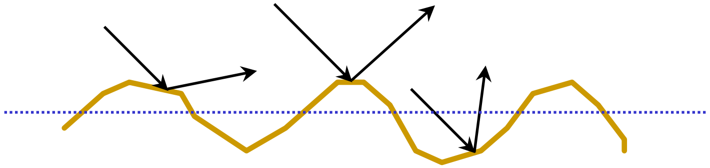
Effect of Crystallinity on reflectivity



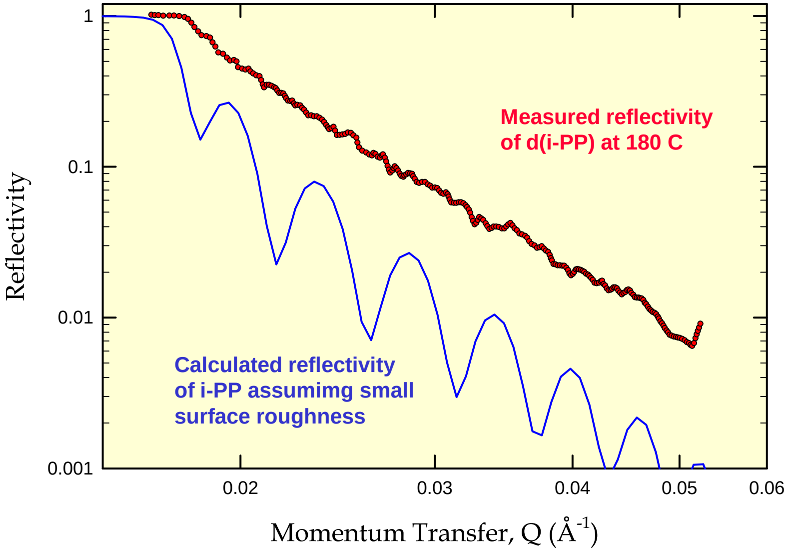
Surface profile of i-PP at RT



Brewster angle micrograph of surface of i-PP (bar 20μm)



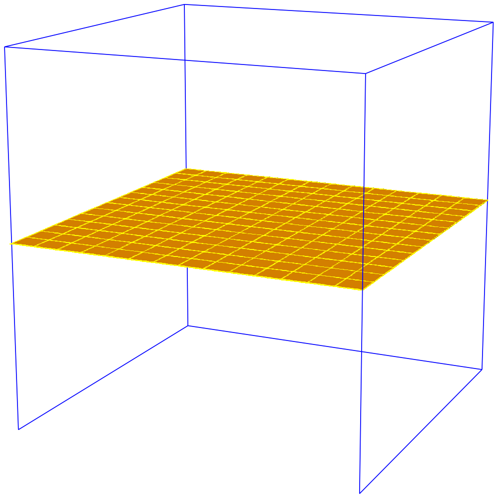
Roughness causes off-specular scattering and increased resolution term.



Measured reflectivity of d(i-PP) at 180 C

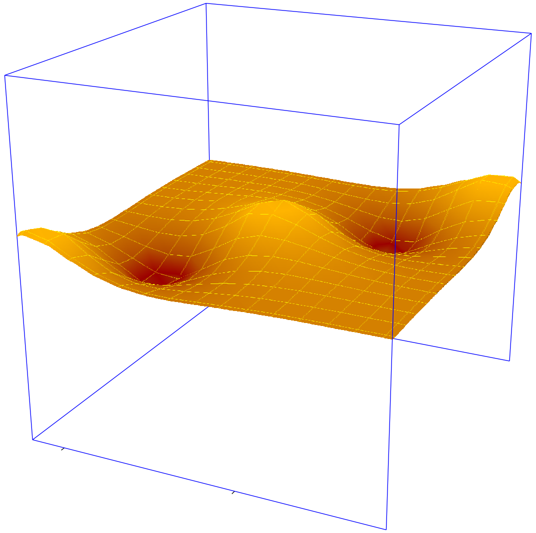
Calculated reflectivity of i-PP assumimg small surface roughness

Thermally Excited Capillary Waves

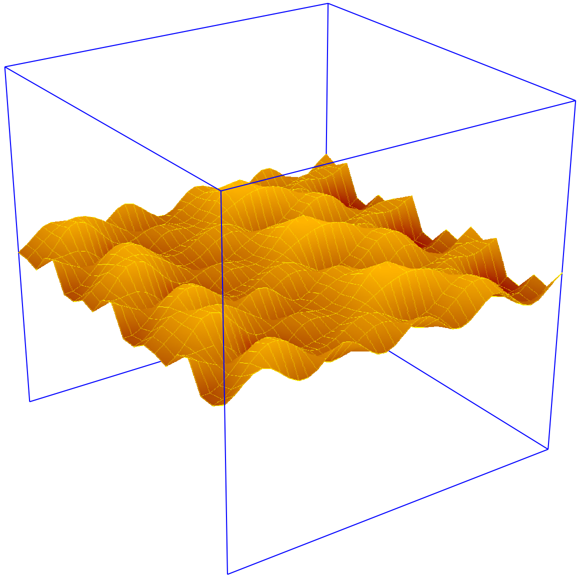


Mean field theory assumes that the interface is flat.

At equilibrium capillary waves are thermally excited.

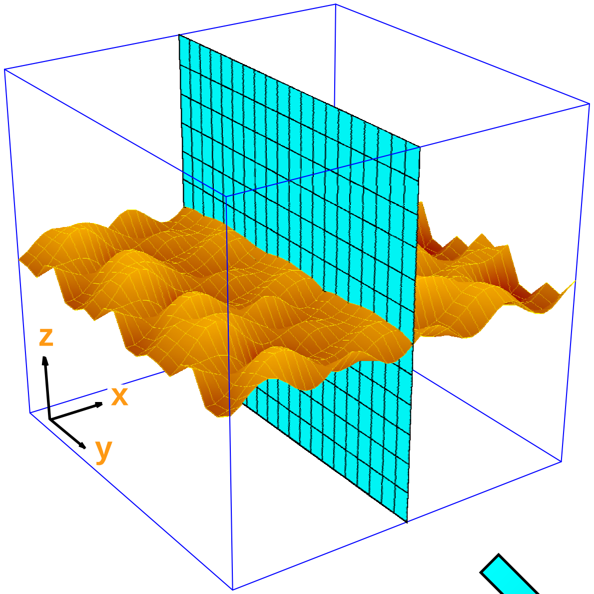


According to the equipartition theorem each mode increases the surface energy by 0.5 kT.



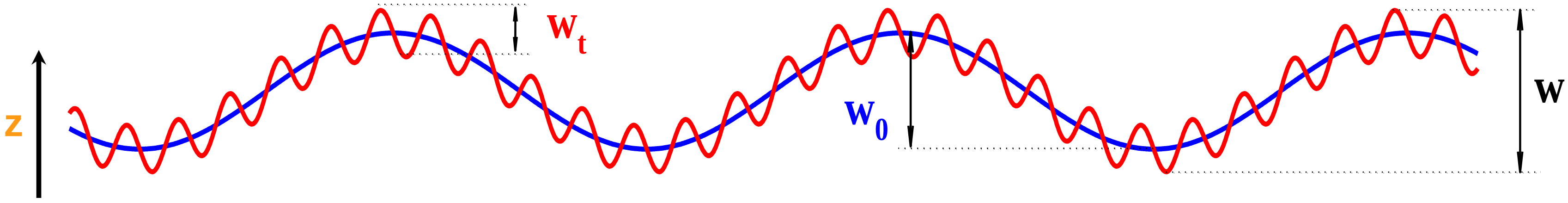
The actual surface is roughened by a superposition of all possible capillary wave modes.

NR Measured Interfacial Width



$$w = (w_t^2 + w_0^2)^{0.5}$$

Definition of w_0 dominates derivation of w_t

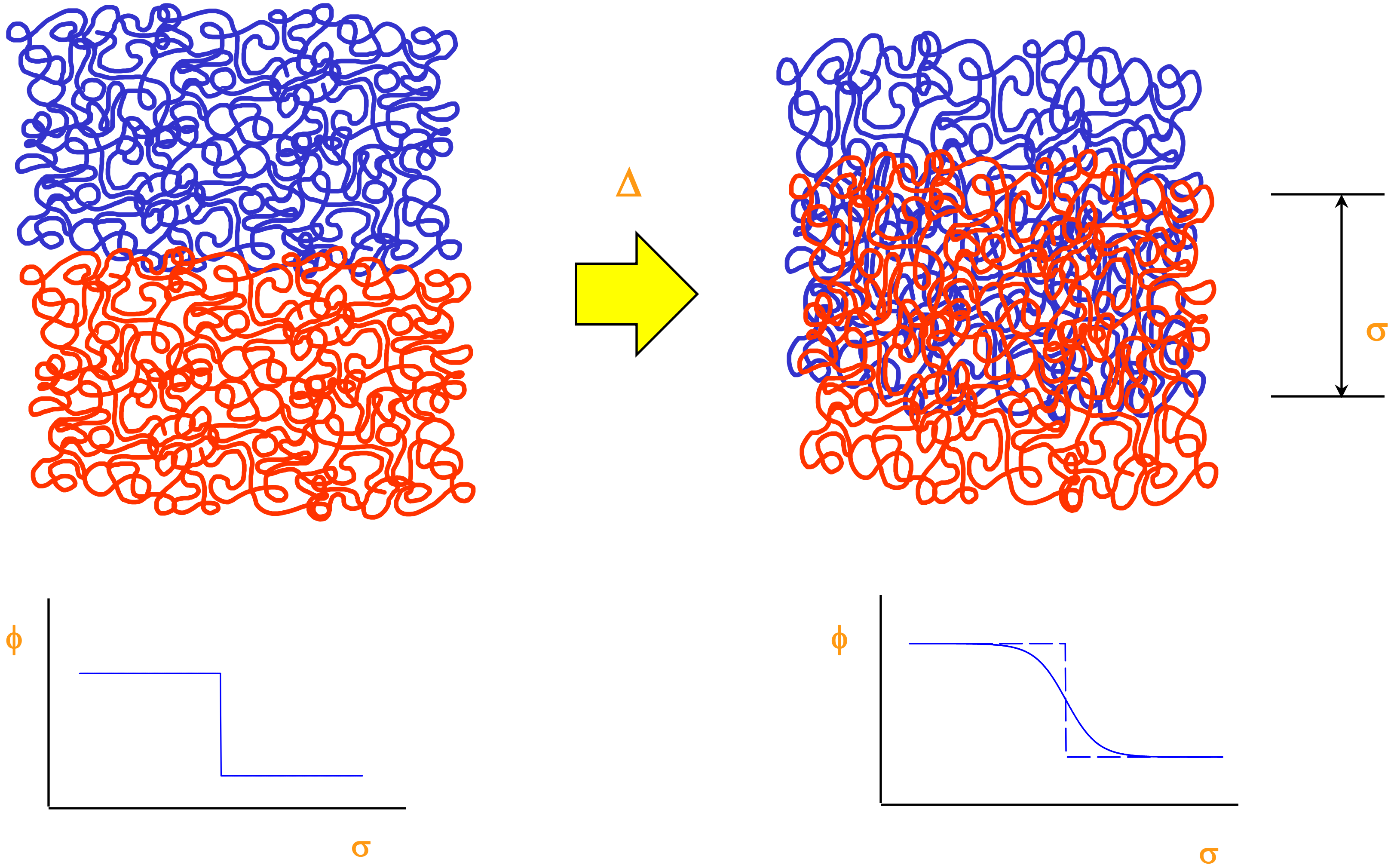


Projection onto z-y plan

Polymer Interdiffusion

As made
t = 0

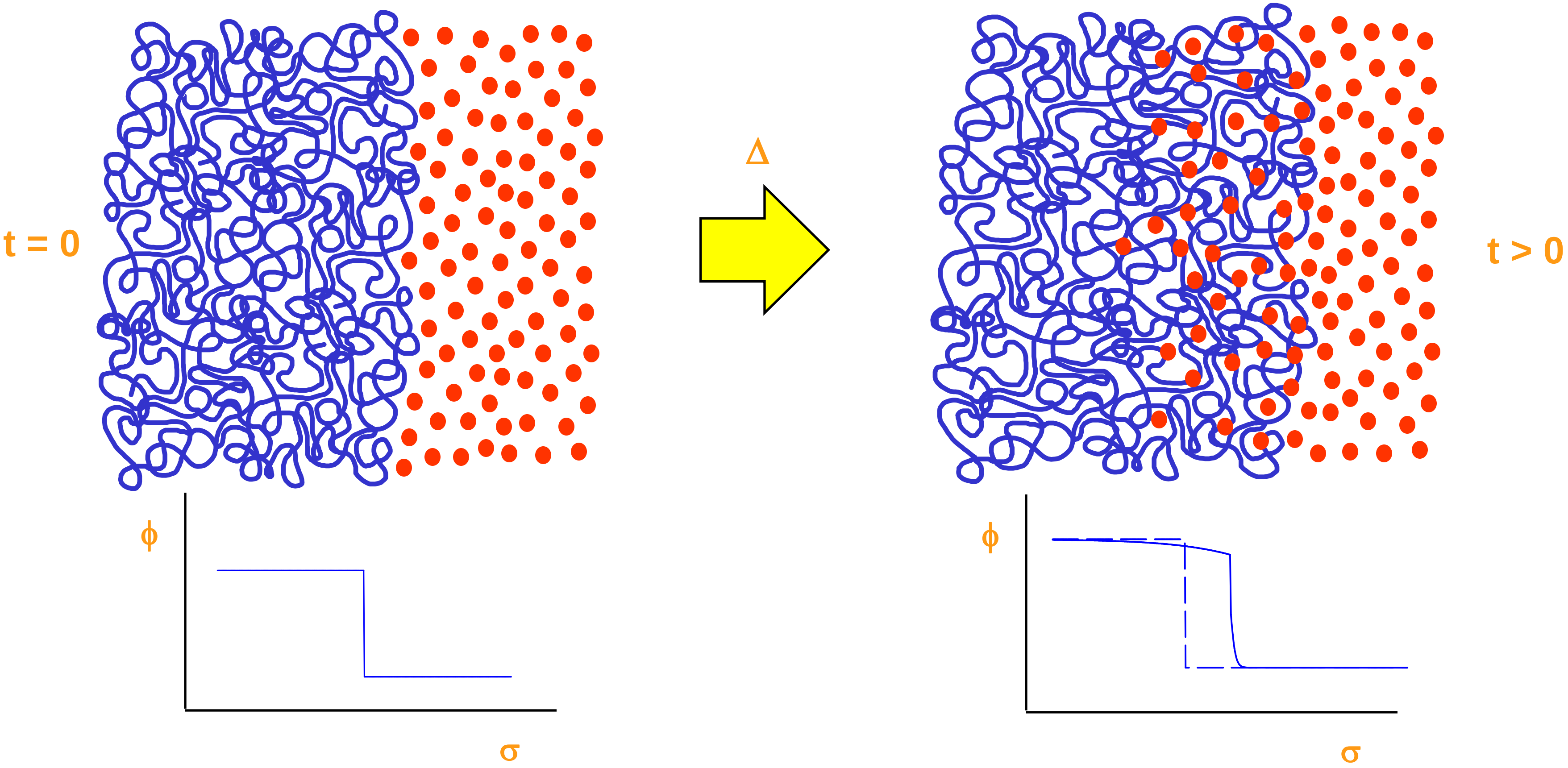
Annealed
t > 0



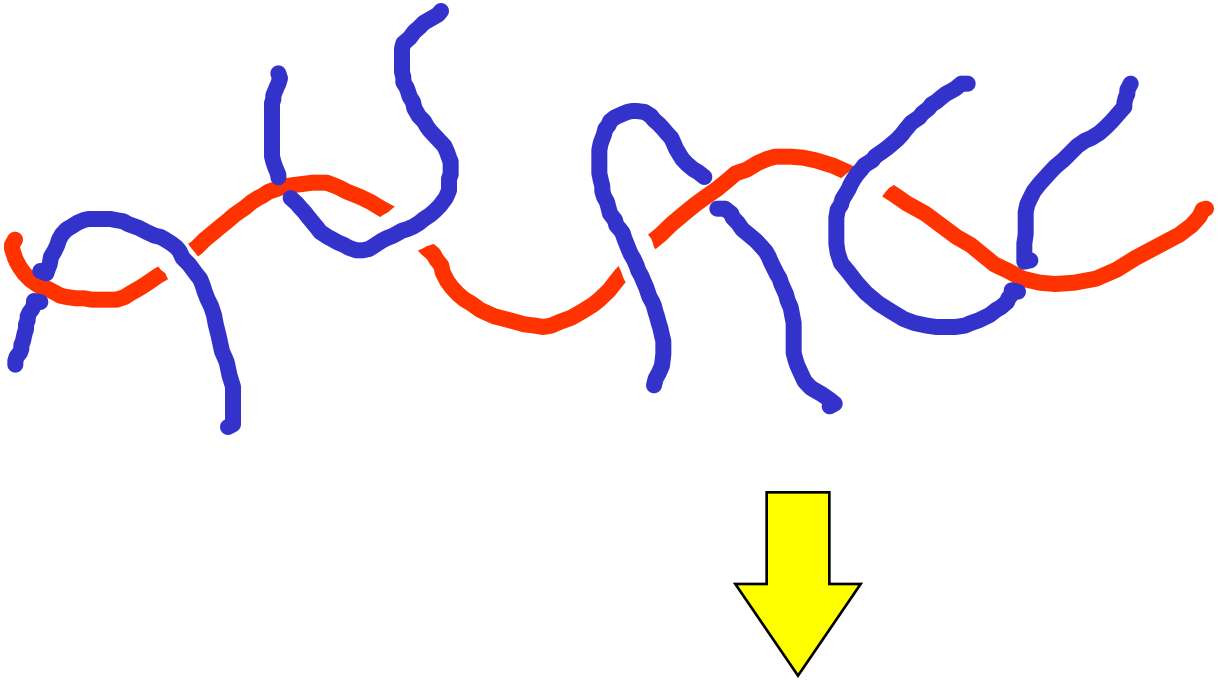
Non-Fickian Diffusion - Case II Diffusion

$$\sigma \propto t^{n} \qquad n \neq \frac{1}{2}$$

Non-Fickian Diffusion

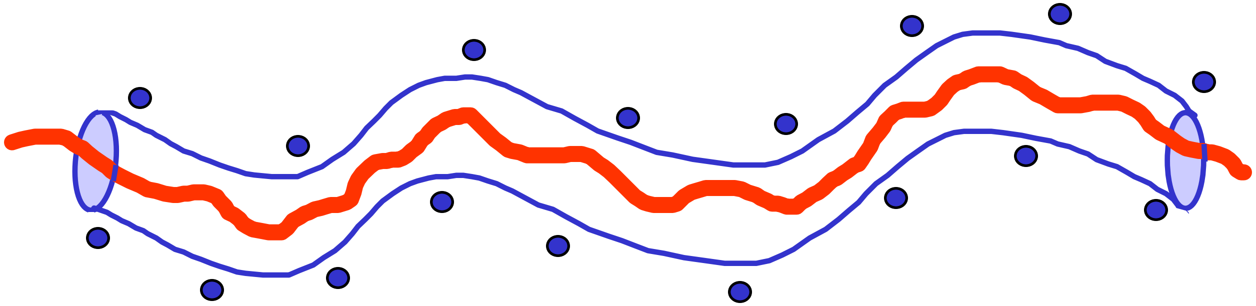


The Tube Model

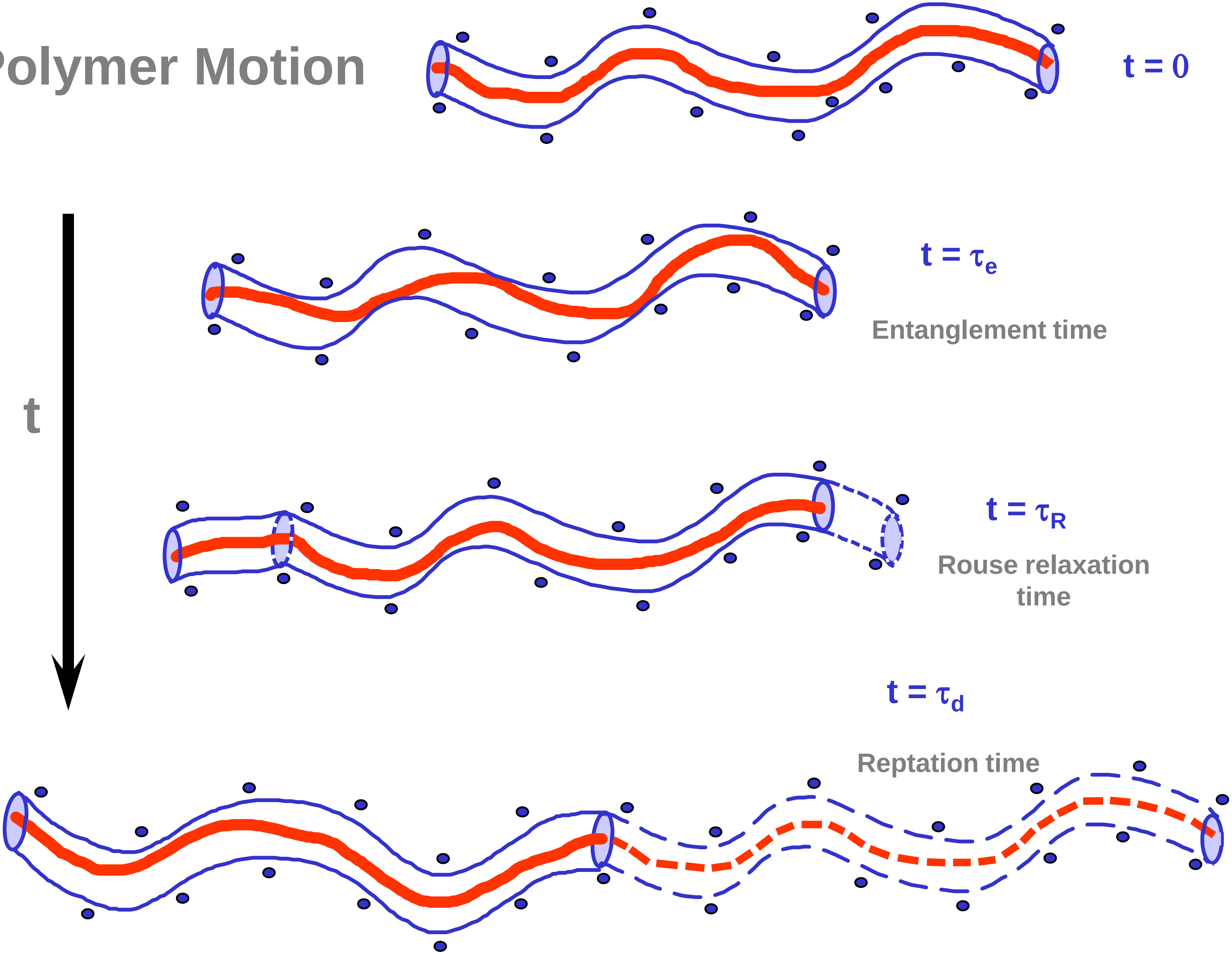


Polymer chains in the melt

Each chain can be considered to be constrained within a tube



Polymer Motion



t

t = 0

t = τ_e

Entanglement time

t = τ_R

Rouse relaxation time

t = τ_d

Reptation time

Polymer Diffusion

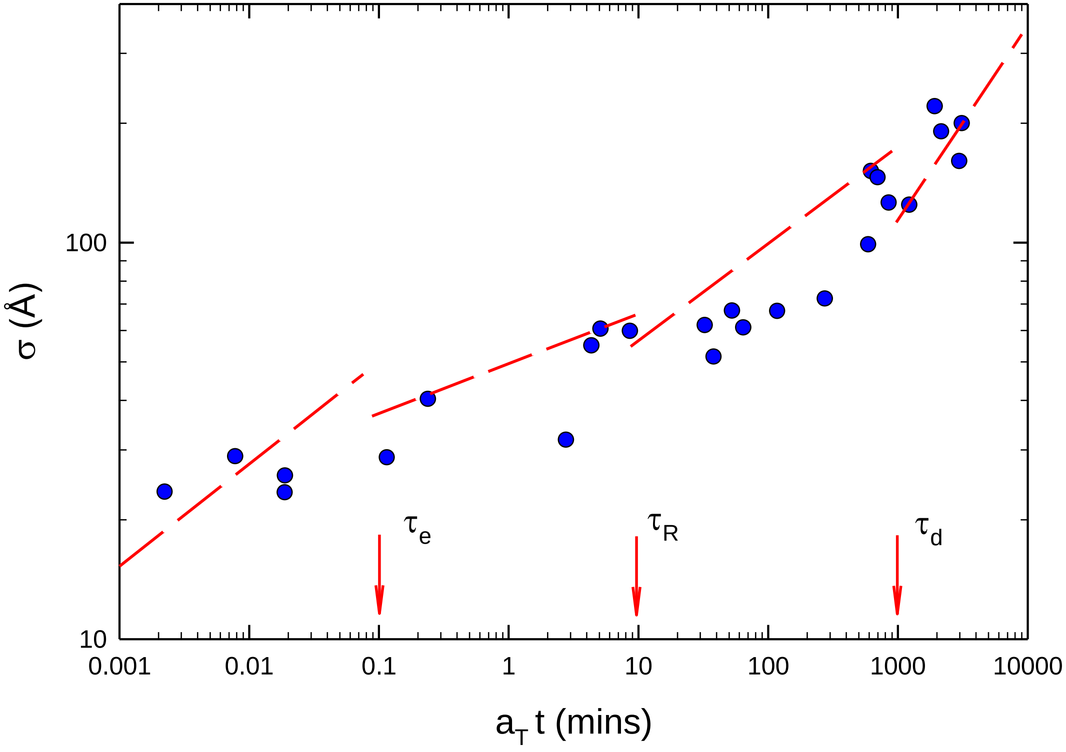
$t < \tau_e$ ⇒ $\sigma \infty t^{1/4}$

$\tau_e < t < \tau_R$ ⇒ $\sigma \infty t^{1/8}$

$\tau_R < t < \tau_d$ ⇒ $\sigma \infty t^{1/4}$

$t > \tau_d$ ⇒ $\sigma \infty t^{1/2}$

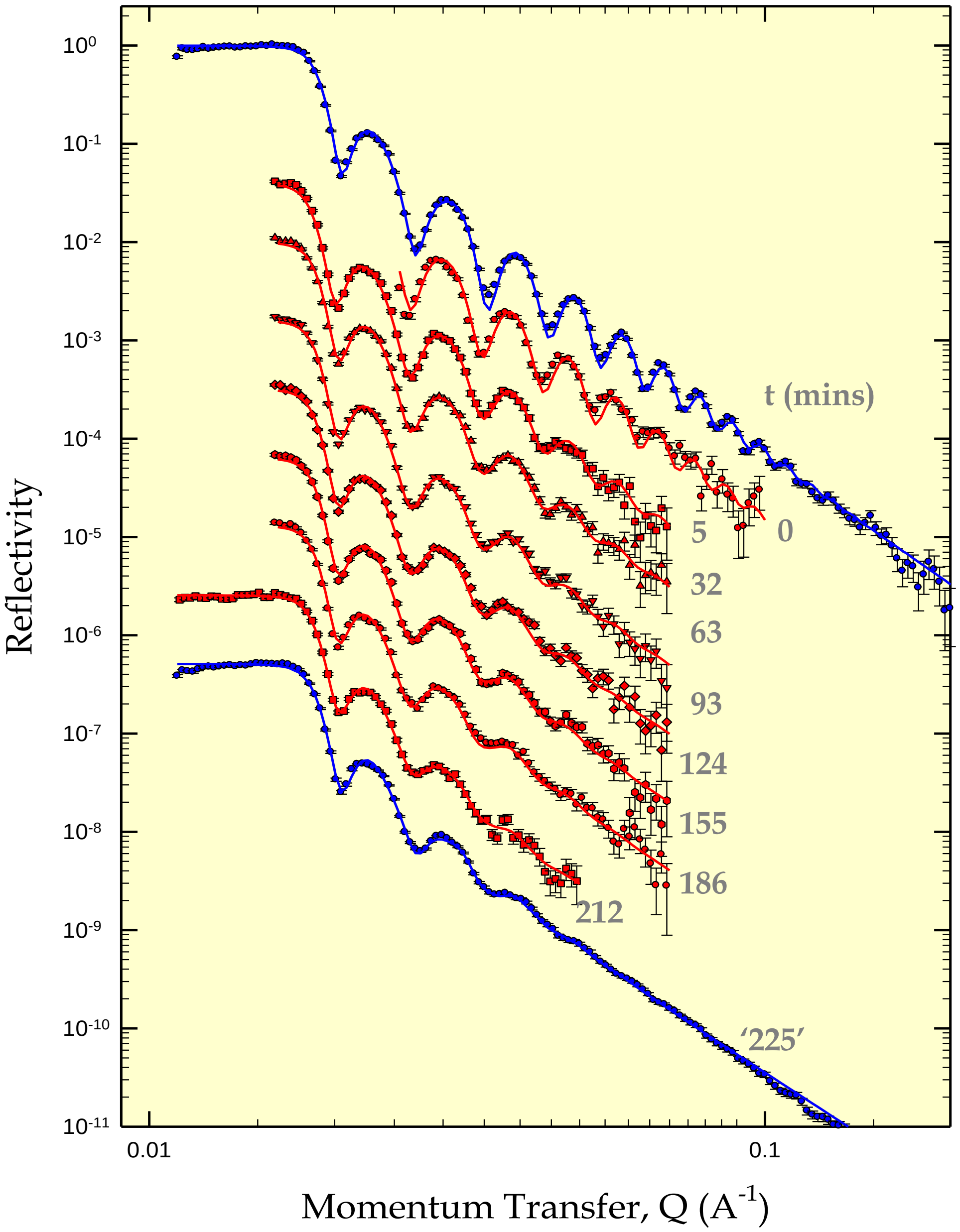
NR Results



A Karim et al, Phys Rev B 42 (1990) 6846

Real Time Reflectivity Measurements

Si / PS (50k) / dPS (40k) @ 115 C



Calculating a Diffusion Coefficient

$$w = \sqrt{4Dt}$$

For dPS-PS system:

$$\boxed{D = (1.7 \pm 0.2) \times 10^{-17}\ \mathrm{cm^2 s^{-1}}}$$

$$D = \frac{k_B T d_T^2}{3N^2 \zeta b^2}$$

M Doi and SF Edwards
The Theory of Polymer Dynamics (1986)

$$D = 2.81 \times 10^{-17}\ \mathrm{cm^2 s^{-1}}$$

When ζ (115C) = 0.199 dyne.s.cm^{-1}
and d_T = 5.7 nm

Reptation time:

$$\tau_r = \frac{Nb^2}{3\pi^2 D}$$

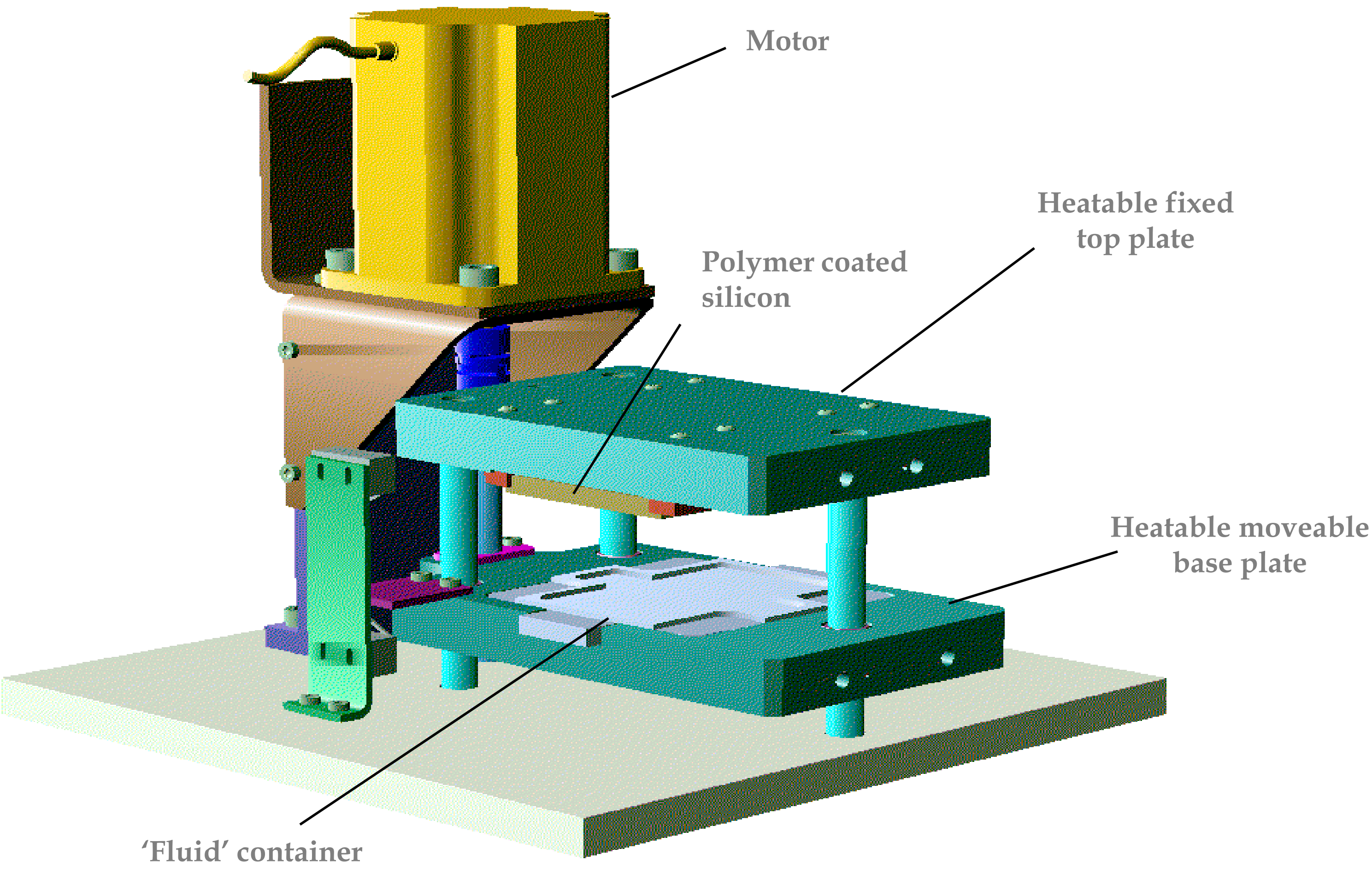
$$\boxed{\begin{aligned}\tau_r &= 3223 \pm 363\ \mathrm{s\ (dPS)} \\ &= 4333 \pm 489\ \mathrm{s\ (hPS)}\end{aligned}}$$

Rouse time:

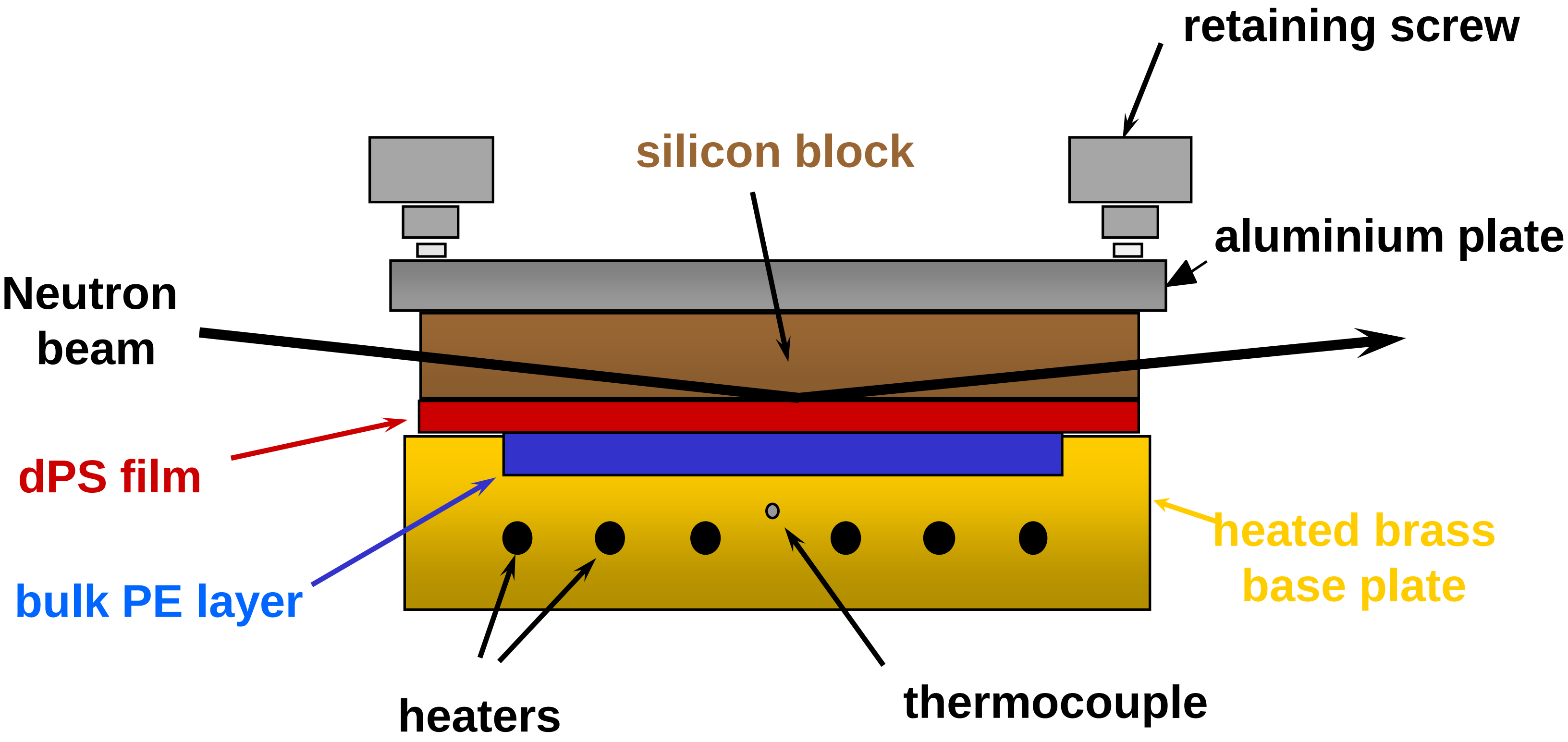
$$\tau_R = \frac{d_T^2}{9\pi^2 D}$$

$$\boxed{\tau_R = 215 \pm 23\ \mathrm{s}}$$

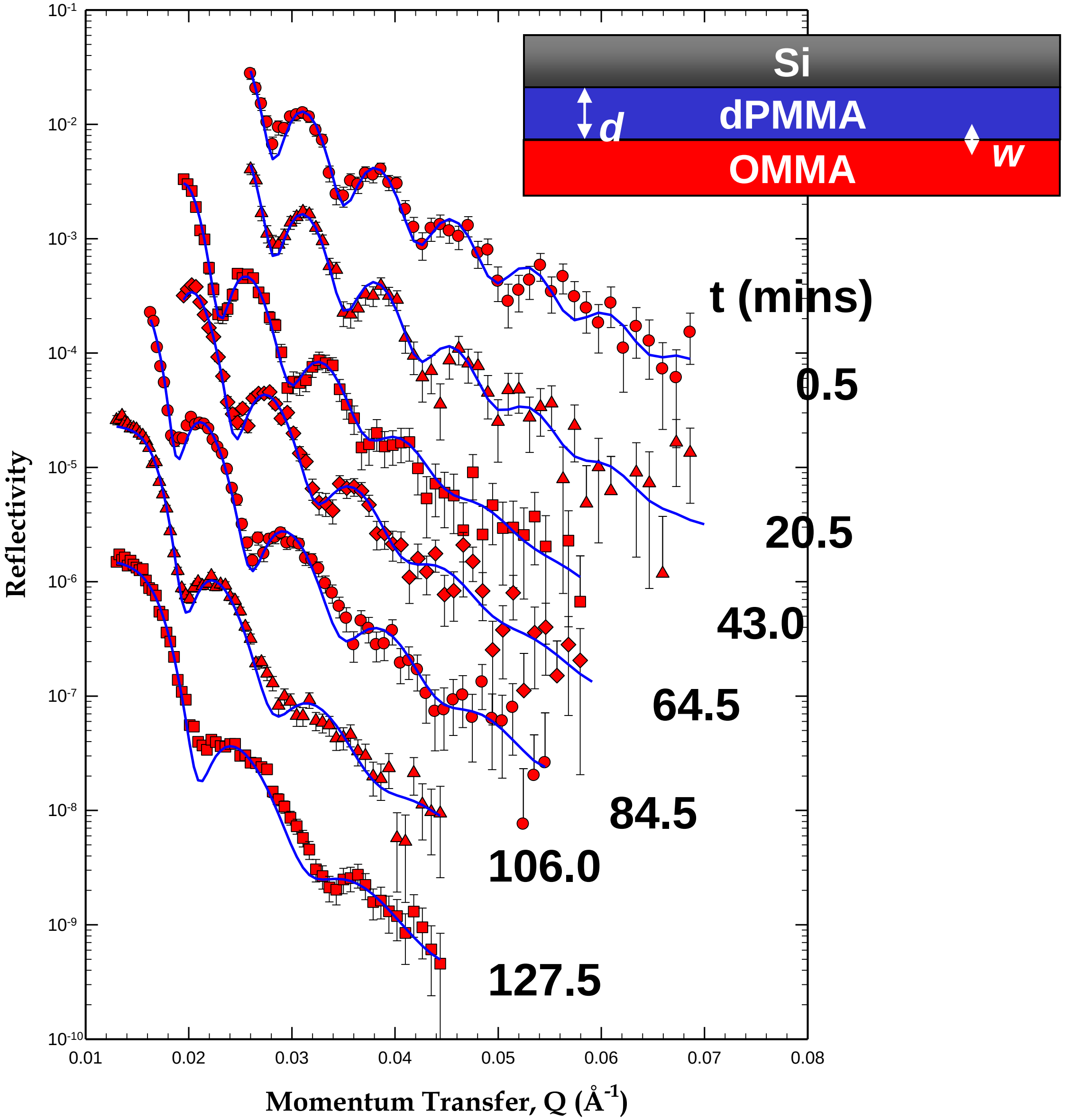
Polymer-Oligomer Interdiffusion Reflectivity Cell



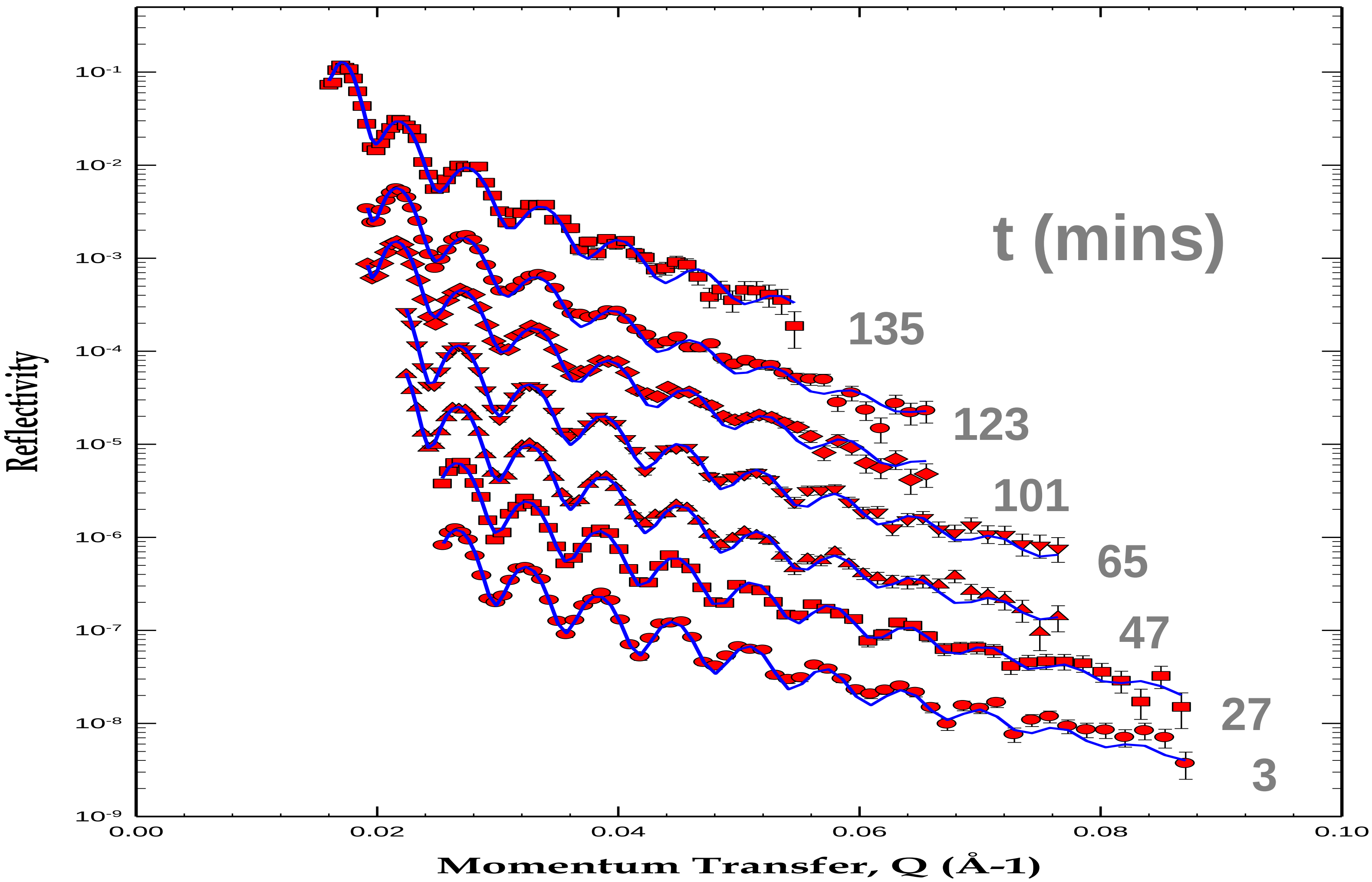
Neutron Reflectivity Melt Cell



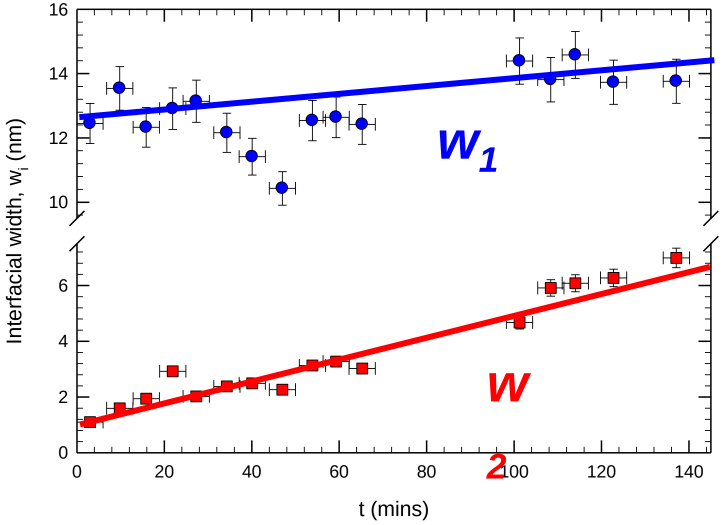
dPMMA(100k) / OMMA(510) @ 45 C

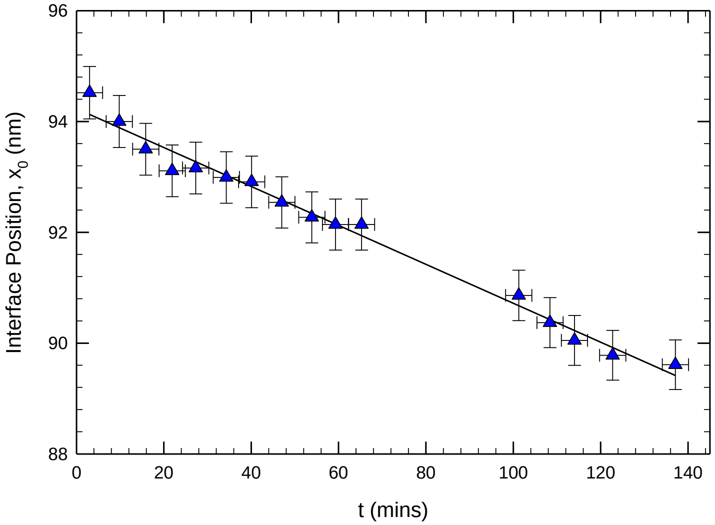


dPS (101k) / OSt (1100) Interdiffusion @ 65C

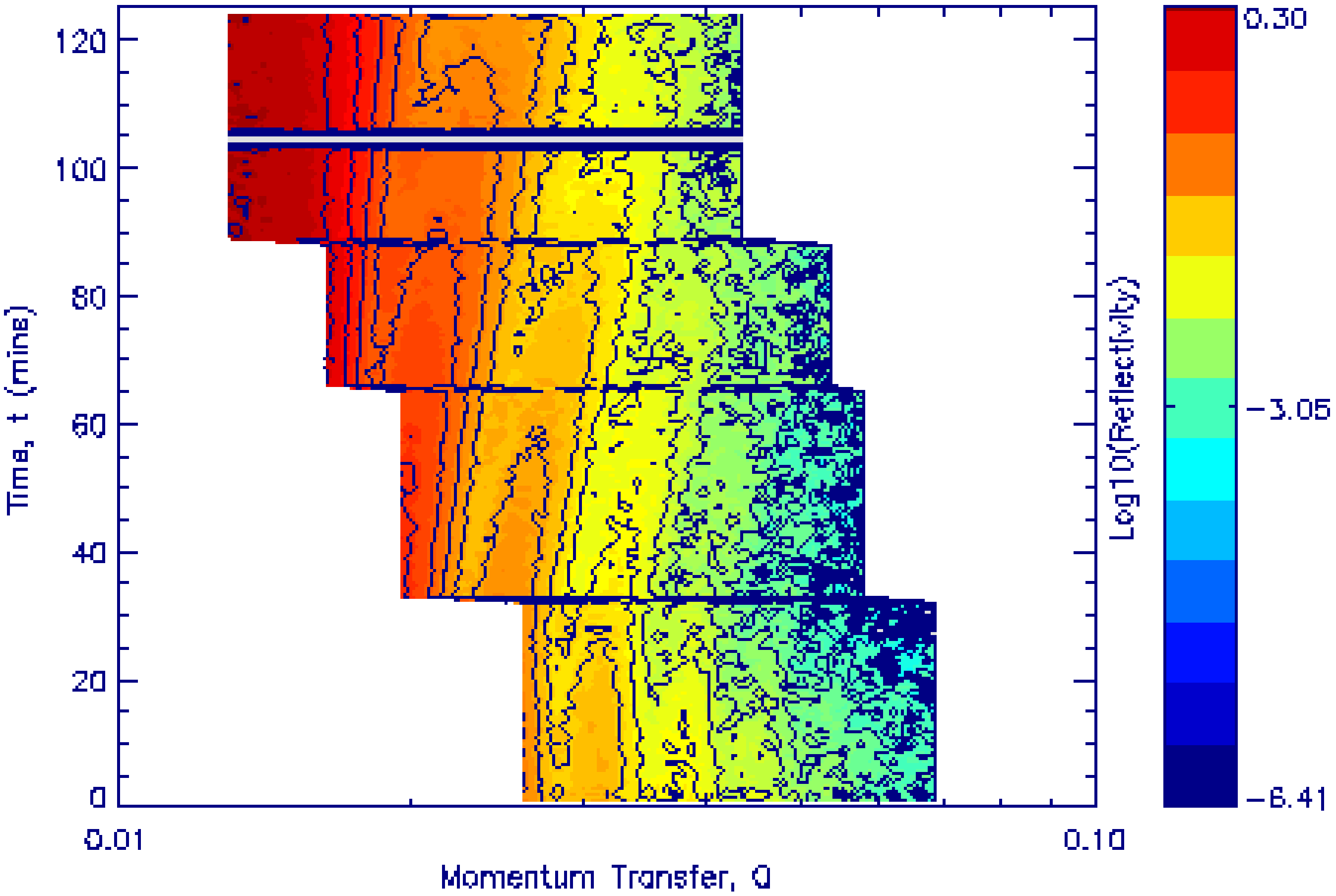


dPS (101k) / OSt (1100) Interdiffusion   @ 65C

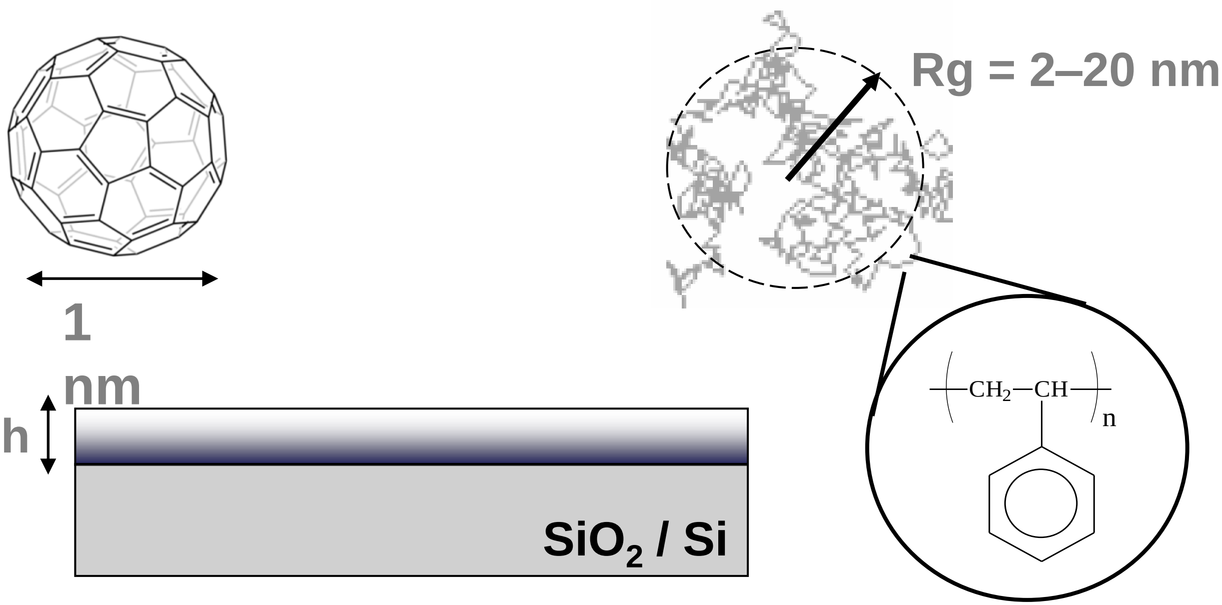




Off-specular reflection



(B) Soft Matter application: depth profiling of nanofilled polymer films



Fullerene C60
0-5% w/w

1 nm

h

SiO_2 / Si

h = 5-500 nm

Rg = 2–20 nm

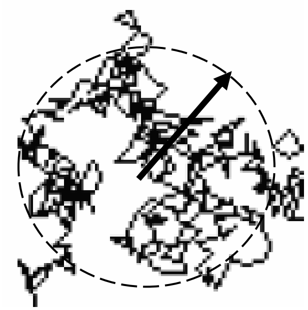
Polystyrene (PS)

Rg=0.27 Mw $^{1/2}$

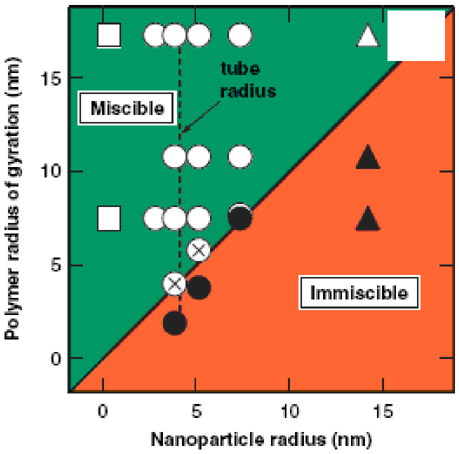
Phys Rev Lett **105, 038301 (2010); *Macromolecules* 43, 9578-9582 (2010); *J. Mol. Liq* 153 79-87 (2010); *Macromolecules* (2010 ASAP)**

Polymer-fullerene ‘mixtures’

Fullerene C_{60}

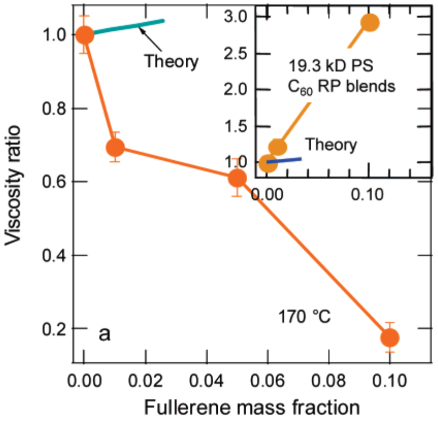


Polystyrene (PS)



Mackay et al. Science (2006) 311, 1740

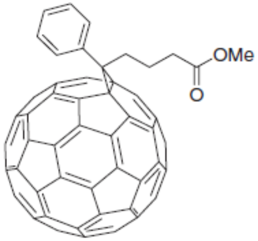
Transport properties



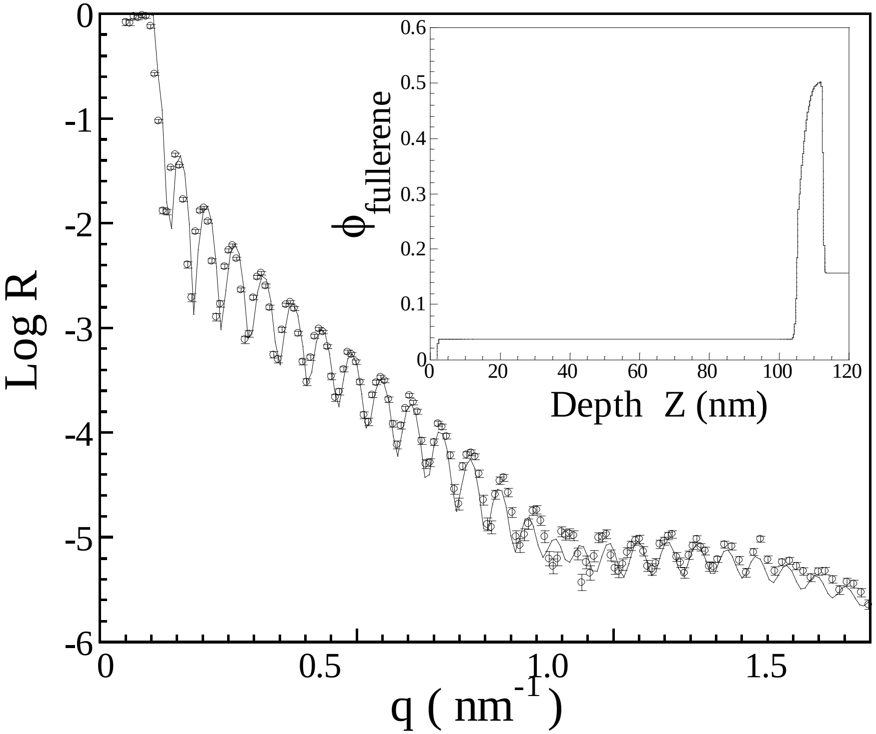
Tuteja et al. Nat. Mat. (2003) 2, 762

Electrical properties

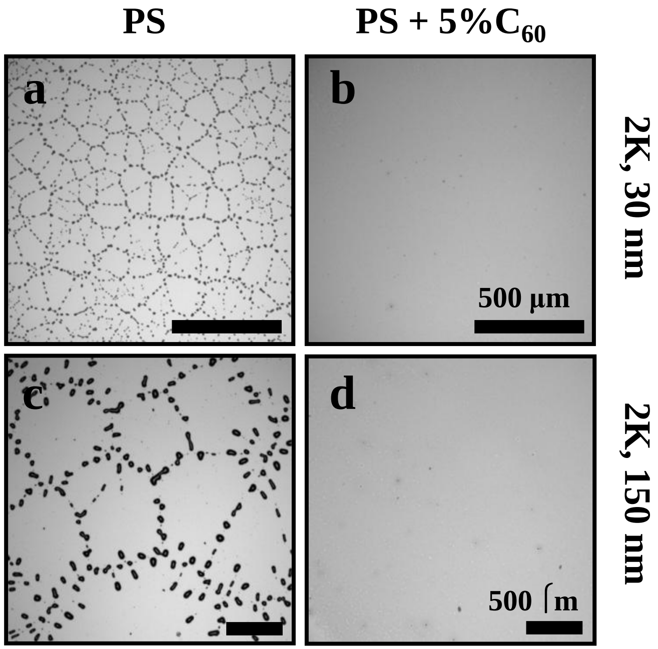
Fullerene derivative (PCBM)



Heegar et al. Adv. Funct. Mater (2005) 15, 1617



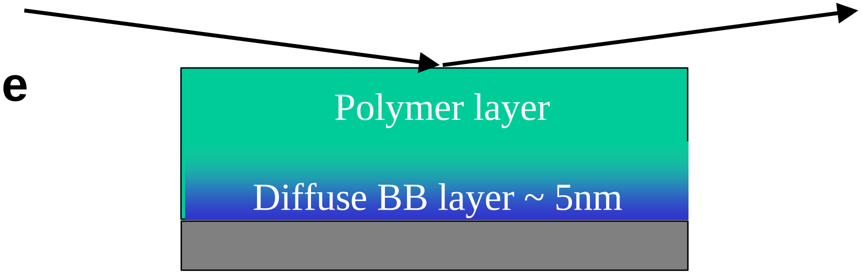
PS+5% C60 h = 100nm



140ºC

180ºC

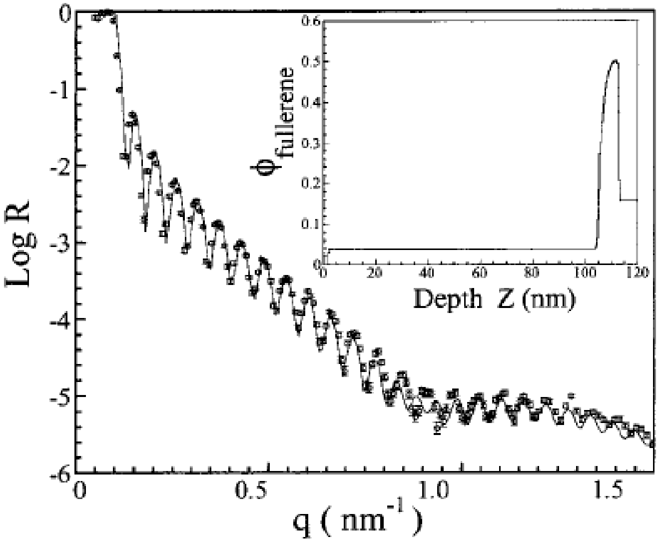
- Neutron reflection from PS containing 5% fullerene on Si



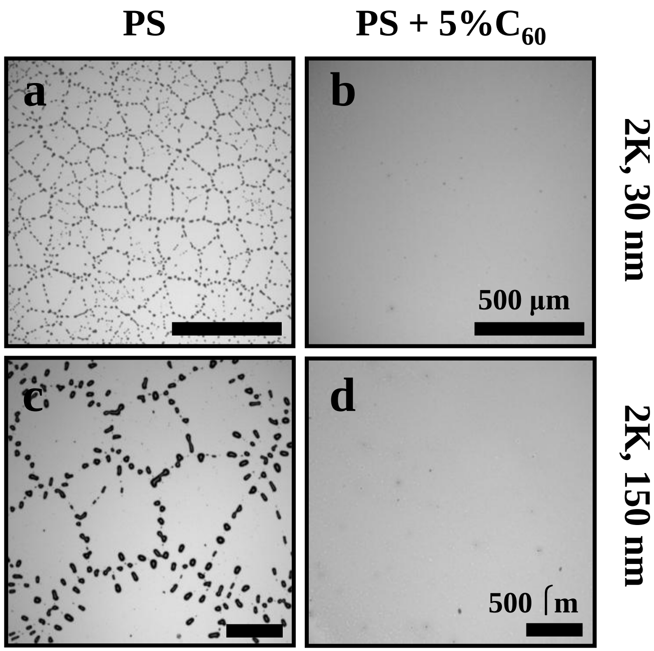
Polymer layer

Diffuse BB layer ~ 5nm

- Fullerenes not present at air surface (confirmed water contact angle)
- Segregation of 2-5 nm thick *diffuse* layer of fullerenes on Si

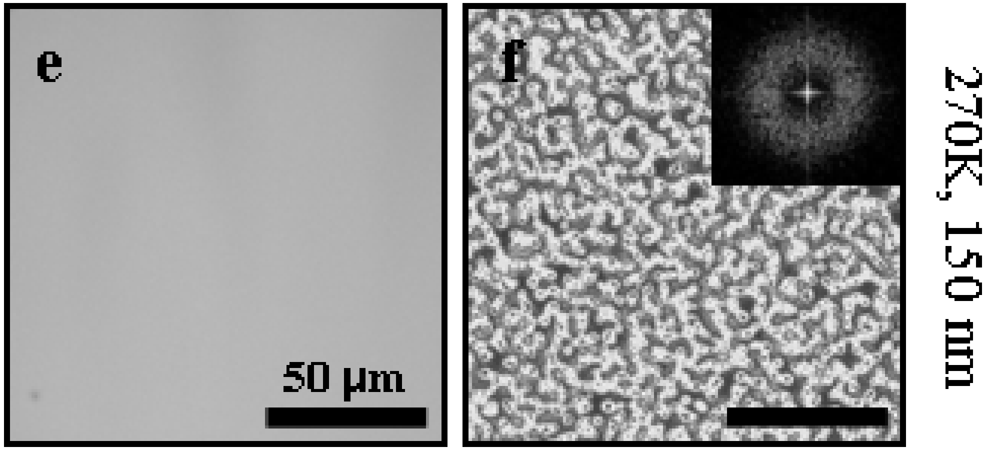


PS+5% C60 h = 100nm



140°C

180°C



180°C

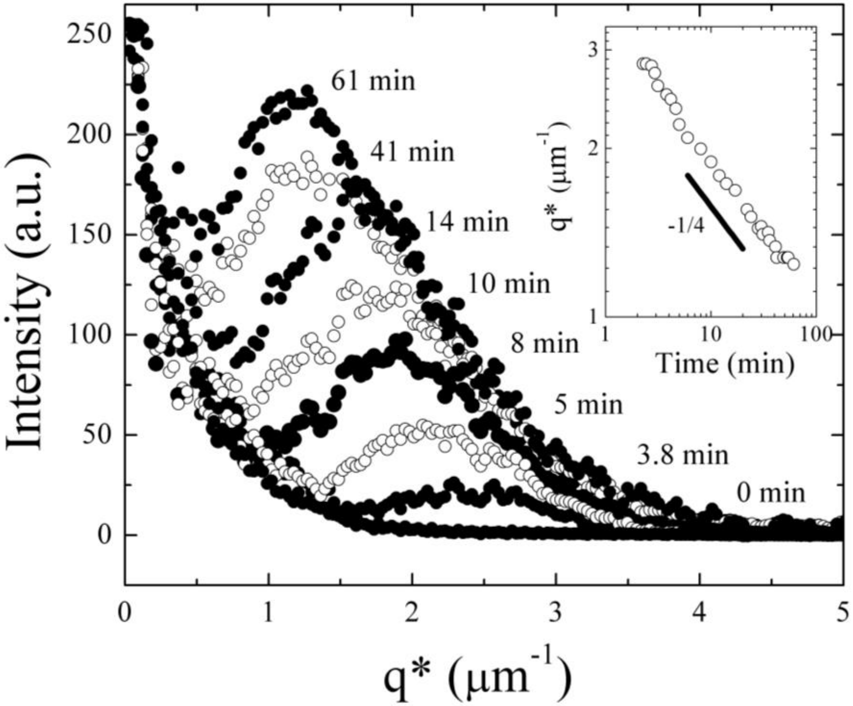
‘Spinodal Clustering’

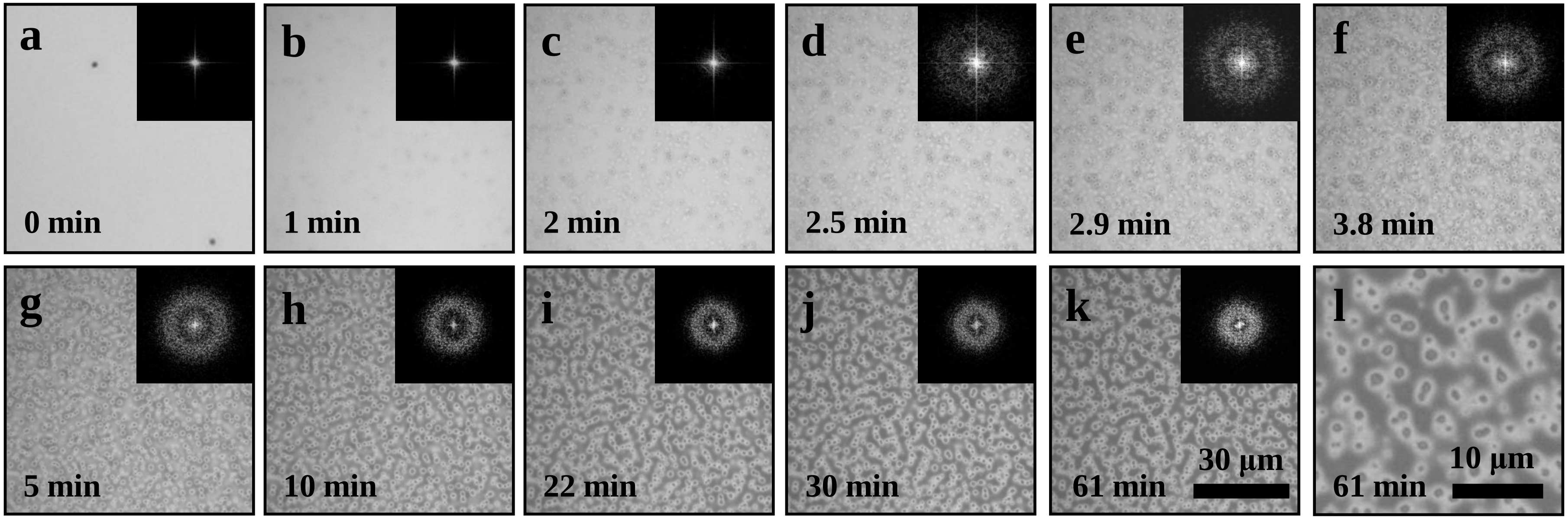
Coarsening Kinetics

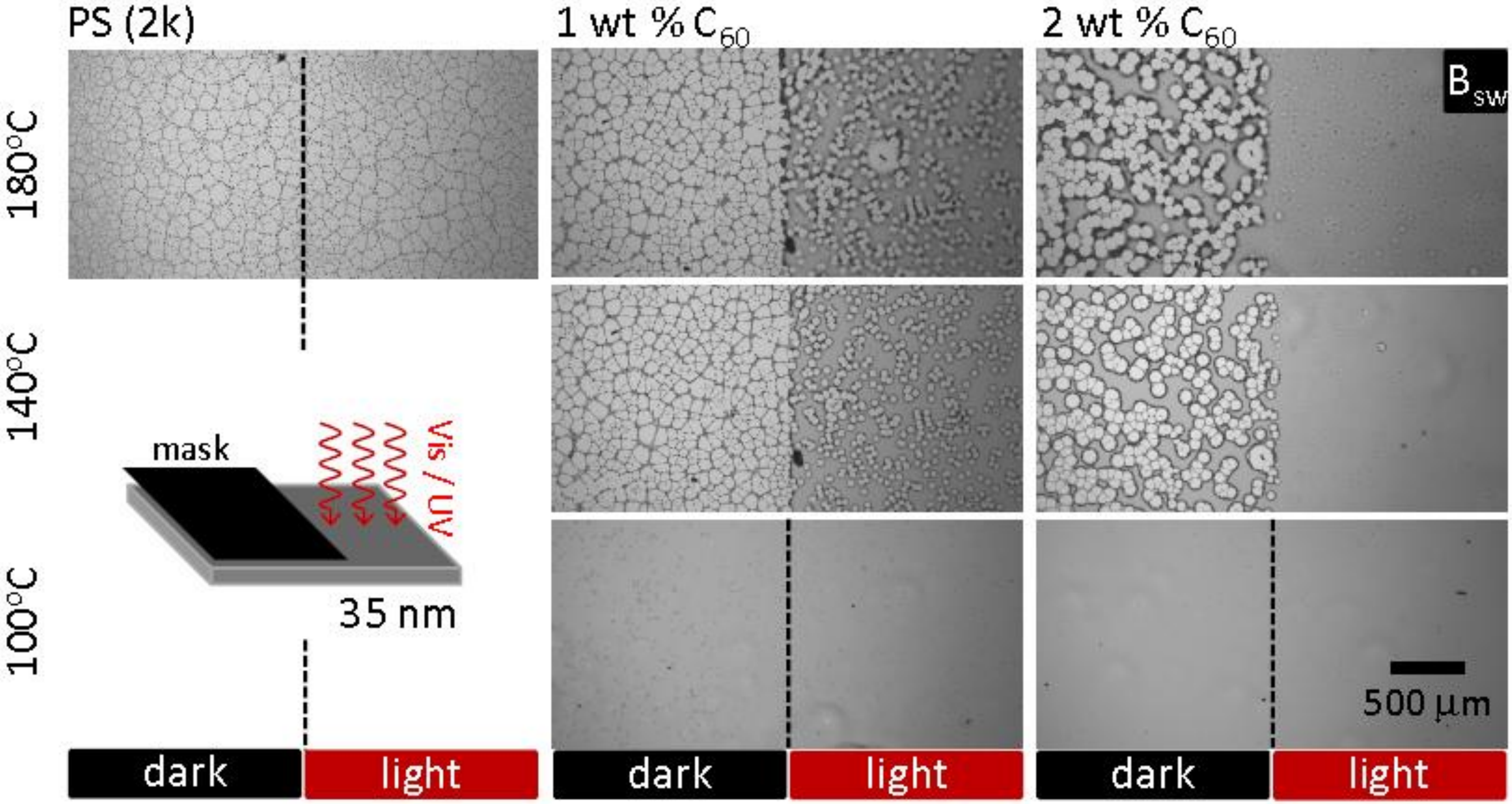
PS+5%C_{60}

170 ^{o}C

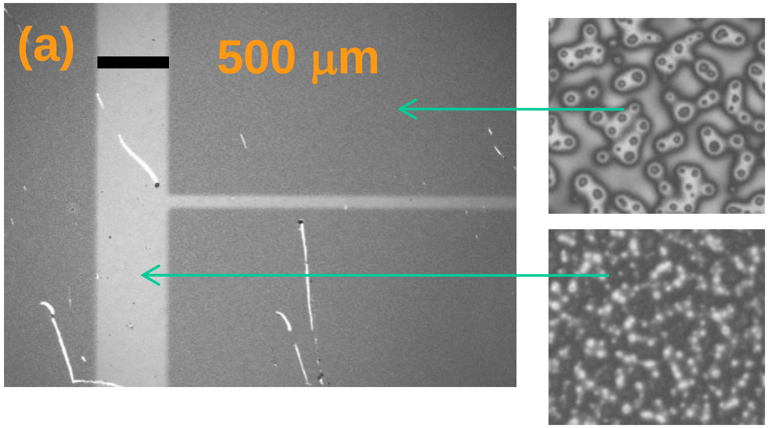
h=160 nm



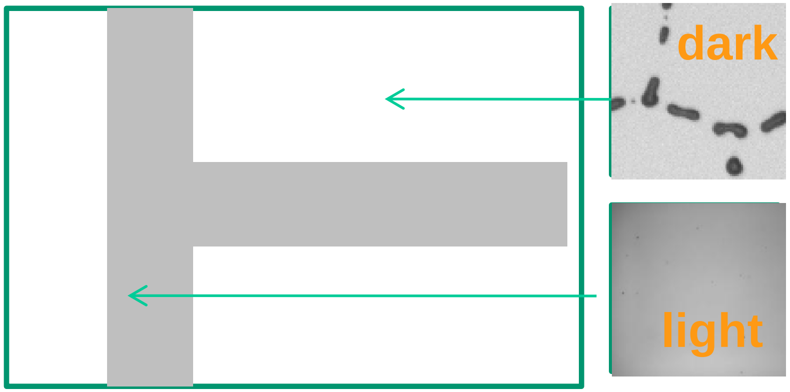


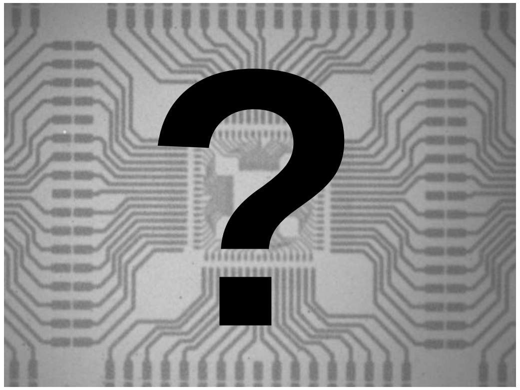

PS (2k)
1 wt % C$_{60}$
2 wt % C$_{60}$
B$_{sw}$
180°C
140°C
100°C
mask
Vis / UV
35 nm
500 μm
dark
light
dark
light
dark
light

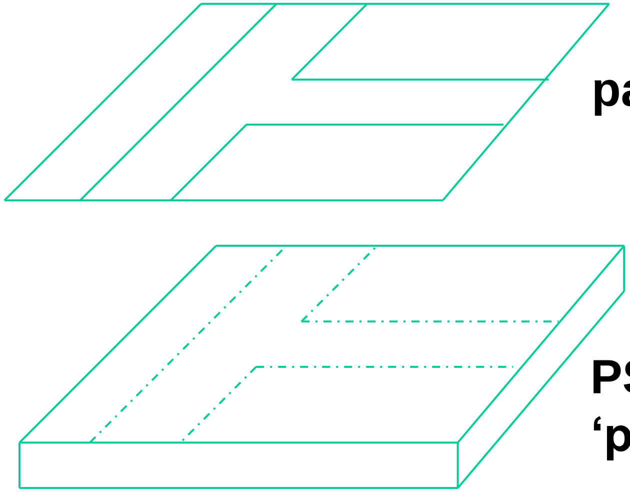
High Mw



Low Mw





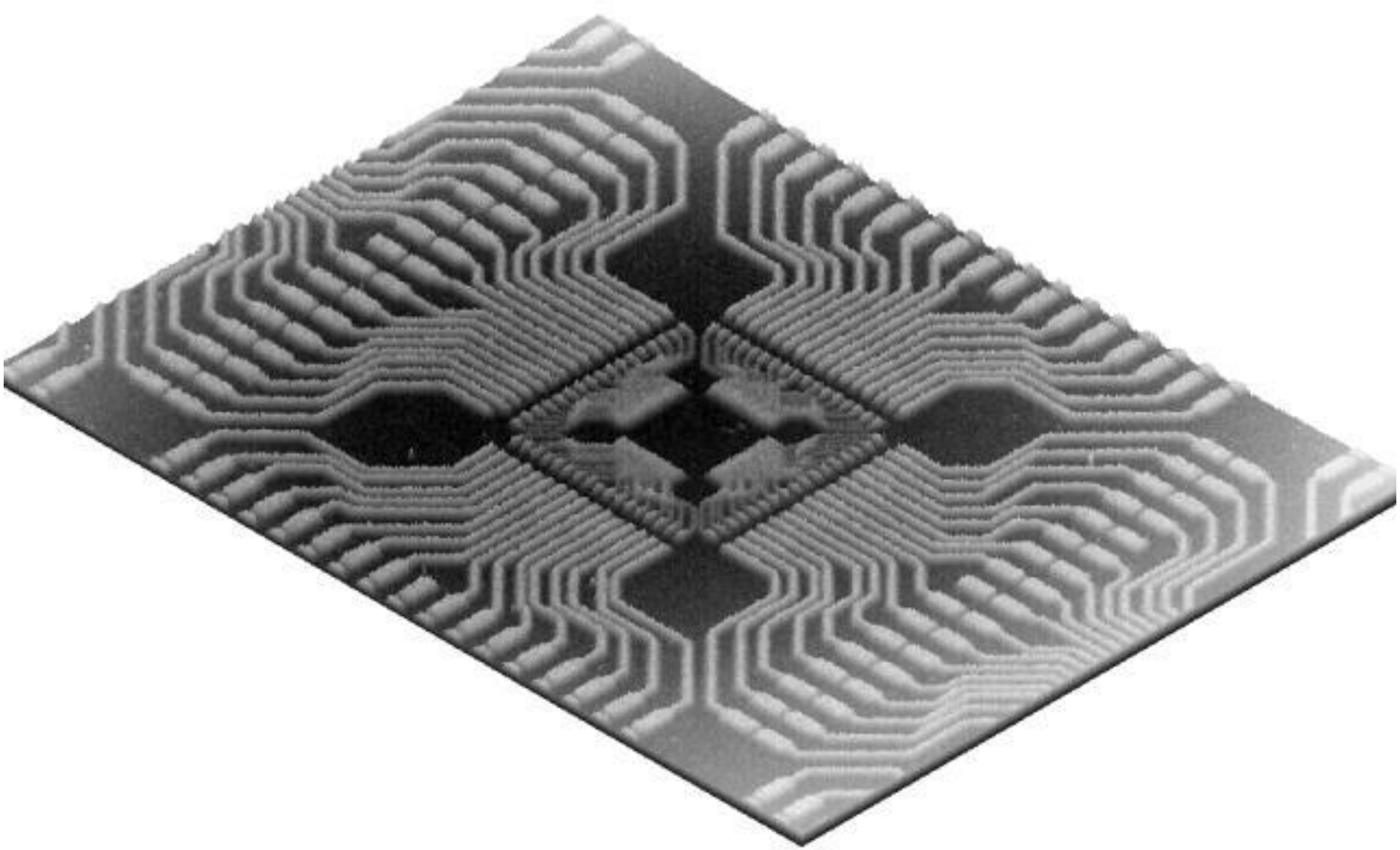


pattern

PS-C60 film
‘photoresist’

Annealing above Tg

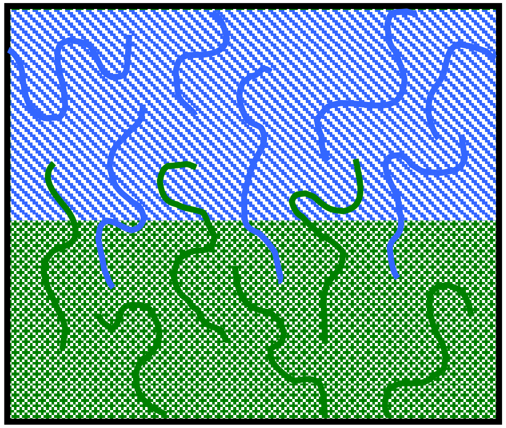
Coupling of self-assembly & patterning



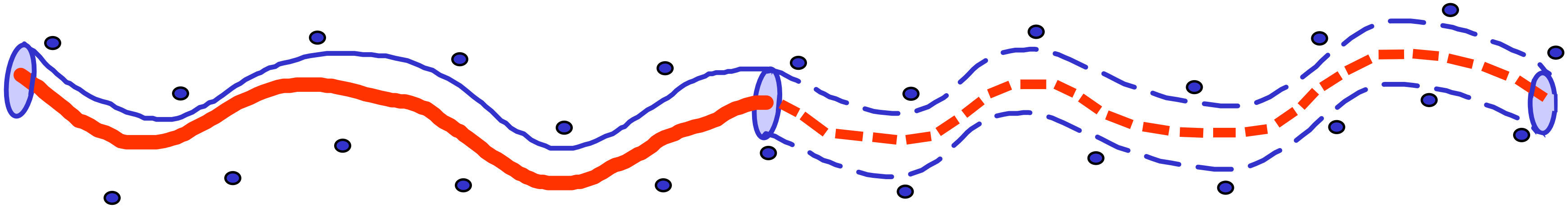
Summary

Reflectivity

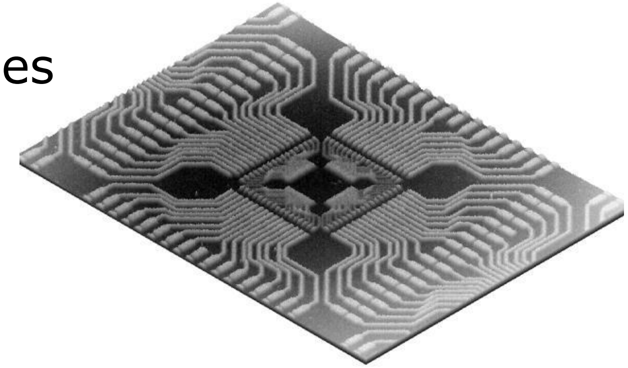
- study and design interfaces



- investigate diffusion mechanisms



- engineer ‘functional’ surfaces / devices



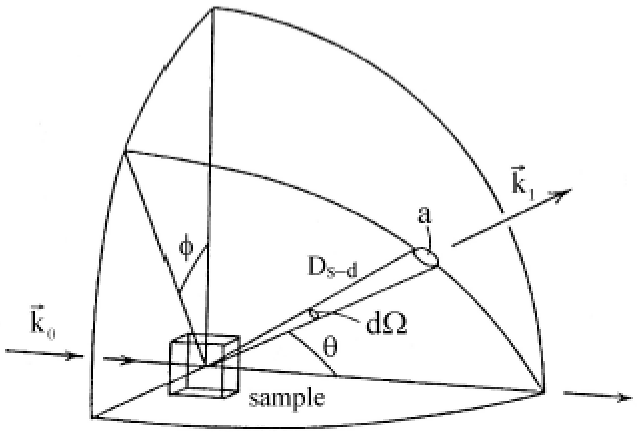
Neutrons in soft matter

Lecture 2 (II) – Dynamics

João T. Cabral
Department of Chemical Engineering
Imperial College London

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

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*)

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

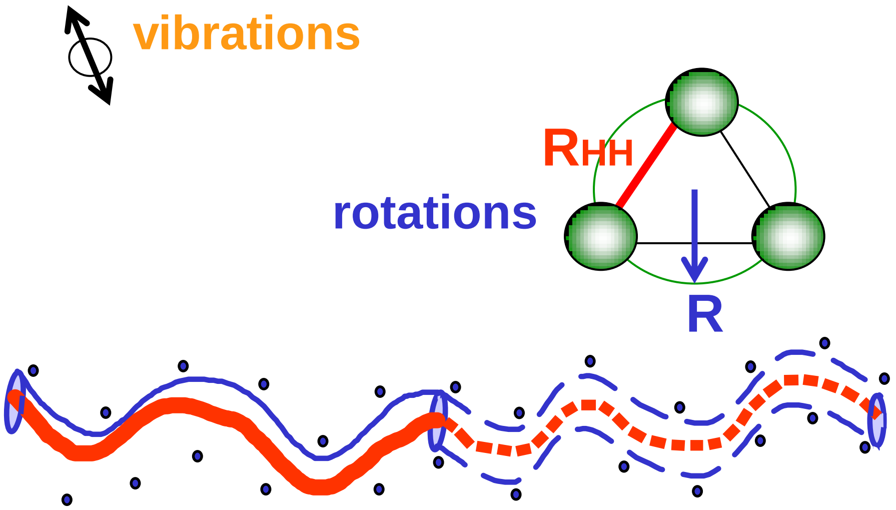
Intermediate scattering function

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

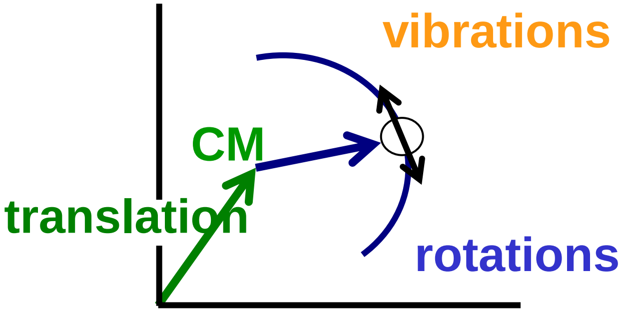
$$G(\mathbf{r},t) = \frac{1}{(2\pi)^3}\int I(\mathbf{q},t)e^{-i\mathbf{q}\cdot\mathbf{r}}d\mathbf{q}.$$



vibrations

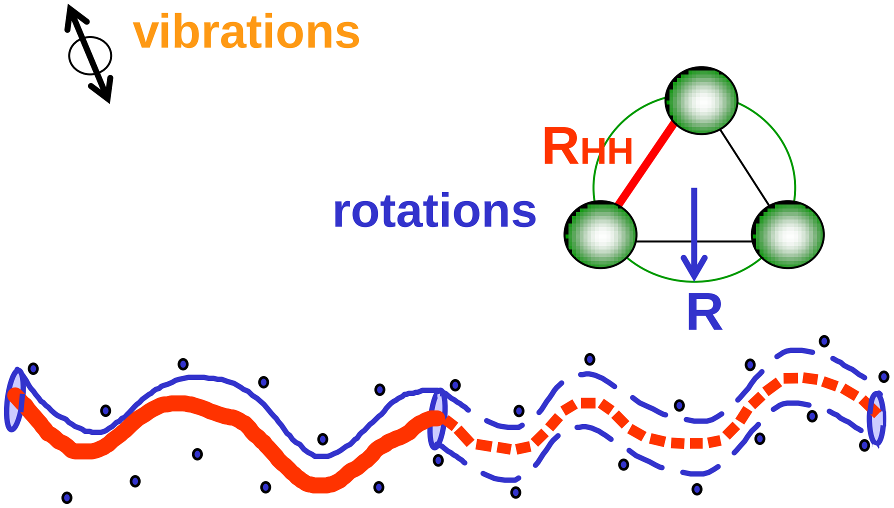
rotations

single-particle dynamics

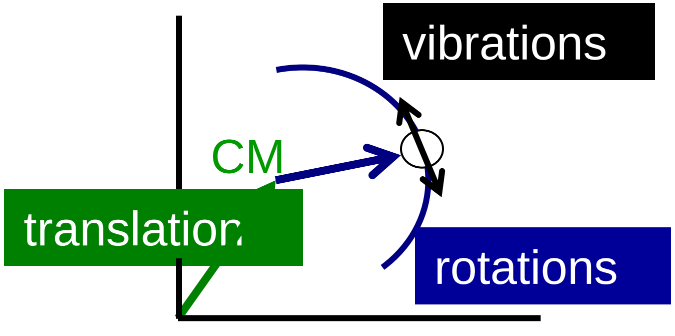


motion decomposition

$$I_{self}(Q,t)=\frac{1}{N}\sum_i\left\langle e^{iQ\bullet[V(t)-V(0)]}\right\rangle\left\langle e^{iQ\bullet[T(t)-T(0)]}\right\rangle\left\langle e^{iQ\bullet[R(t)-R(0)]}\right\rangle$$



single-particle tools


vibrations

translation

rotations

motion decomposition

$$I_{self}(Q,t)=\frac{1}{N}\sum_i\left\langle e^{iQ\bullet[V(t)-V(0)]}\right\rangle\left\langle e^{iQ\bullet[T(t)-T(0)]}\right\rangle\left\langle e^{iQ\bullet[R(t)-R(0)]}\right\rangle$$

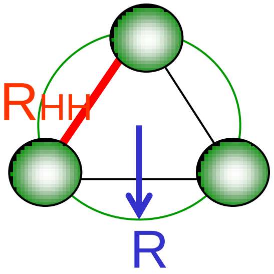
CM translation frozen for polymers T<<Tg.

Proton delocalisation DW factor: $e^{-\frac{1}{3}Q^2\langle u^2\rangle}$

relevant proton reorientations: methyl and phenyl rotations about group's axis.

Methyl protons 3-fold jumps

R ≈1.032 Å



$$S_{rot}(Q,\omega)=A_0(Q)\delta(\omega)+A_1(Q)\frac{1}{\pi}\frac{3/2\tau}{(3/2\tau)^2+\omega^2}$$

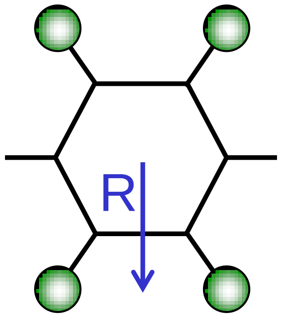
with
$$A_0(Q)=\tfrac{1}{3}\left[1+2j_0(Qr\sqrt{3})\right]$$
$$A_1(Q)=1-A_0(Q)$$

Phenyl proton 2-fold jumps

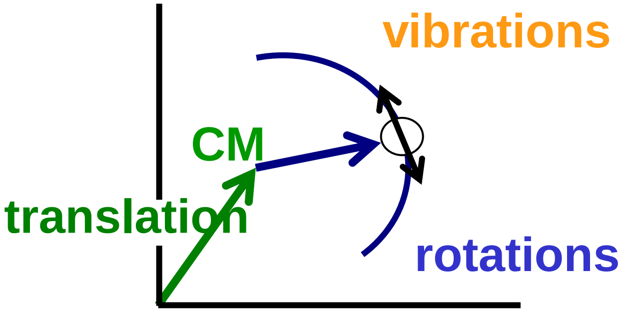
R ≈ 2.28 Å

$$S_{rot}(Q,\omega)=A_0(Q)\delta(\omega)+A_1(Q)\frac{1}{\pi}\frac{2/\tau}{(2/\tau)^2+\omega^2}$$

with $A_0(Q)=\tfrac{1}{2}\left[1+j_0(2Qr)\right]$



single-particle dynamics



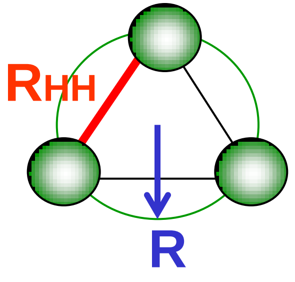
motion decomposition in the glass

CM translation: frozen for polymers T<<Tg.

Proton delocalisation: DW factor: $e^{-\frac{1}{3}Q^2\langle u^2\rangle}$

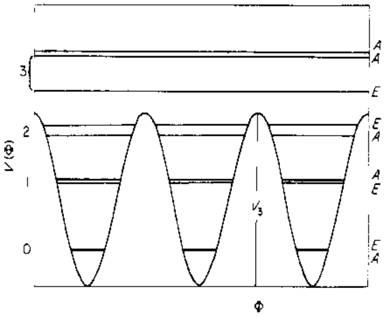
example:

Side group rotations:



R ≈1.032 Å

3-fold CH_3 potential



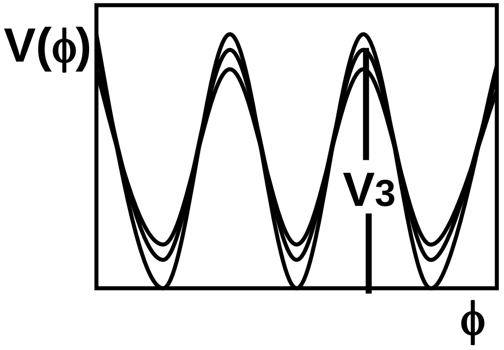
Methyl protons 3-fold jumps

$$S_{rot}(Q,\omega) = A_0(Q)\delta(\omega) + A_1(Q)\frac{1}{\pi}\frac{3/2\tau}{(3/2\tau)^2+\omega^2}$$

with

$$\left| \begin{array}{l} A_0(Q) = \frac{1}{3}\left[1+2j_0(Qr\sqrt{3})\right] \\ A_1(Q) = 1 - A_0(Q) \end{array} \right.$$

distribution $\tau_{correlation}$



glassy polymers: no single relaxation time

variety local environments | **intra-** / **inter-** **molecular**

(Gaussian) distribution of potential barriers:

$$g(E_i) = \frac{1}{\sigma_E\sqrt{2\pi}}\, e^{\frac{-(E_i - E_0)^2}{2\sigma_E^{\,2}}} \qquad \textbf{if} \quad \Gamma = \Gamma_0 e^{-\frac{E_A}{RT}}$$

(log-Gaussian) distribution of reorientation times:

$$g(\ln\Gamma_i) = \frac{1}{\sigma\sqrt{2\pi}}\, e^{\frac{-\ln^2(\Gamma_i/\Gamma_0)}{2\sigma^2}}$$

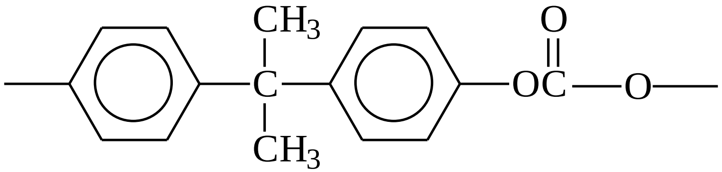
Eo: average barrier height

σ: distribution width

Dynamic structure factor: $S_{rot}(Q,\omega) = A_0(Q)\delta(\omega) + A_1(Q)\sum_{i=1}^{N} g_i L_i(\omega)$

Case study: Polycarbonates

Bisphenol-A polycarbonate

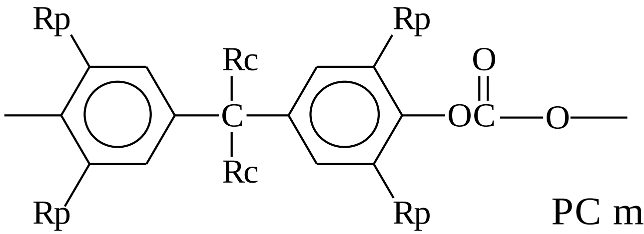


BPA-PC

thermoplastic polymer with remarkable

- optical clarity
- mechanical properties
  - – high $T_{\text{glass transition}}$
  - – large impact strength
  - – ductility.
- commercial applications

depend strongly on architecture



PC modified

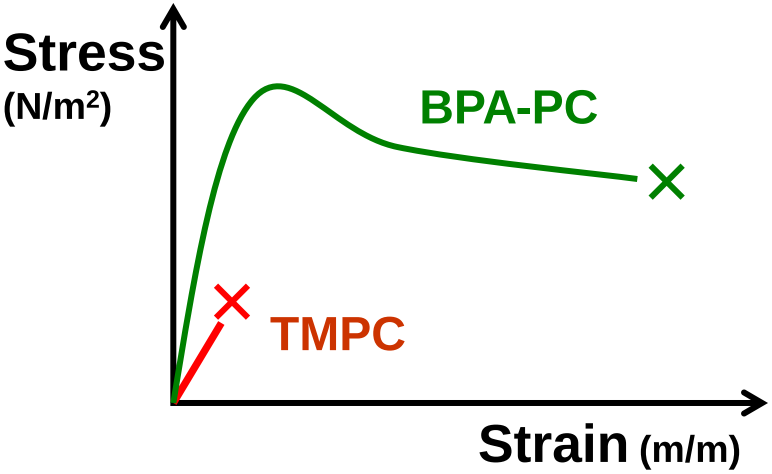
BPA-PC: ~2400 J/m

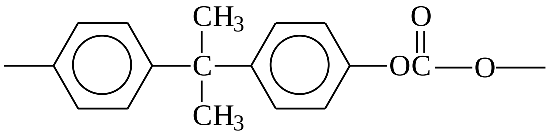
impact strength

(Fried et al. 1990)

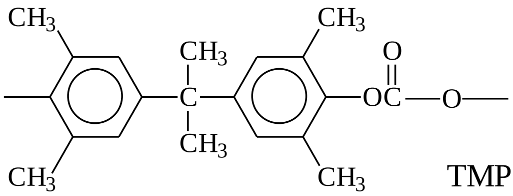
TMPC: ~70 J/m

Toughness





BPA-PC

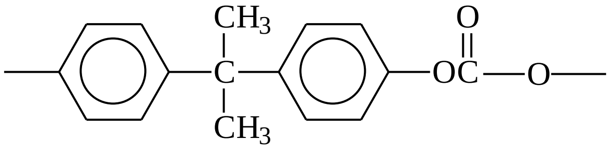


TMPC

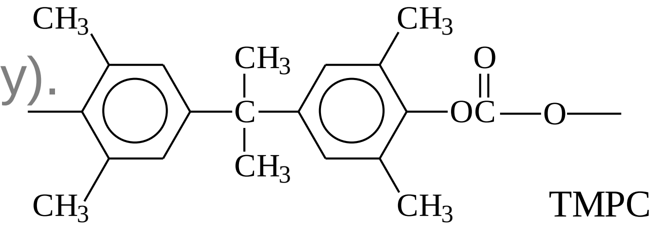
Polycarbonates

Glassy BPAPC

tough → co-operative phenyl motion,
involve ≥1 monomer
(account for dielectric/mechanical activity).



BPA-PC

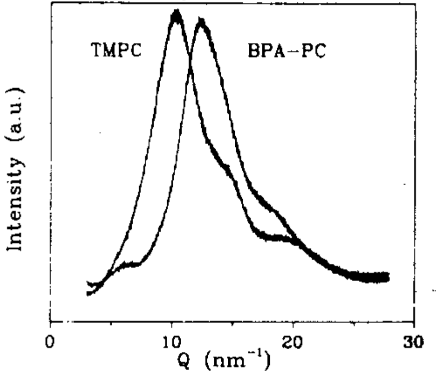


TMPC

Glassy TMPC

most brittle PC → substituted CH_3 hinder backbone mobility;
poor chain packing (large free volume).

Packing



ρ(PC) = 1.198g/cm^3
ρ(TMPC) =1.084g/cm^3

QENS:
characterise dynamics of local reorientation.

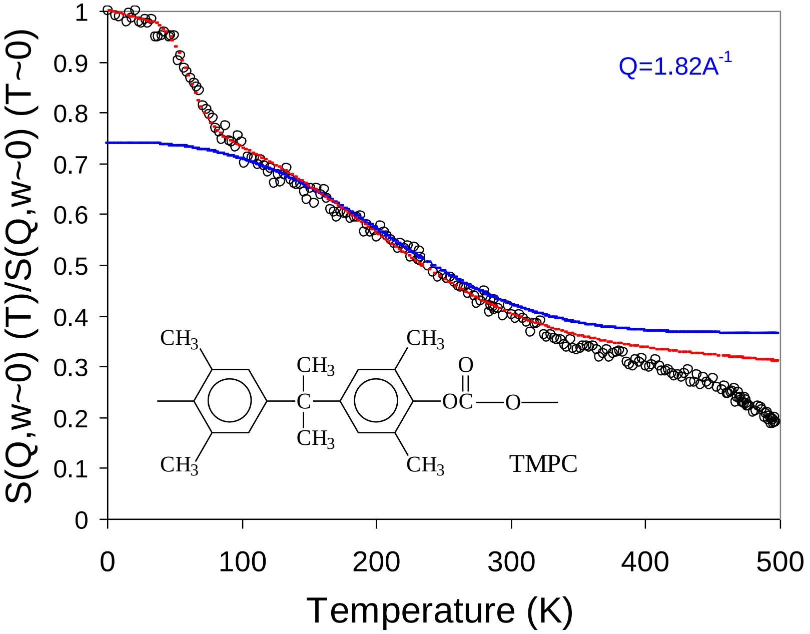
quantitative window scans

Elastic scans

$$S(Q,\omega\sim 0)=\int_{-\infty}^{+\infty} S(Q,\omega')R(\omega-\omega')d\omega'\bigg|_{\omega=0}$$

for a Lorenztian resolution

$$\mathrm{S}(\mathrm{Q},\omega\sim 0)\approx \mathrm{A}_0(\mathrm{Q})+\frac{2}{\pi}\left[1-\mathrm{A}_0(\mathrm{Q})\right]\arctan\left(\frac{\Gamma_{\mathrm{res}}}{\Gamma}\right)$$



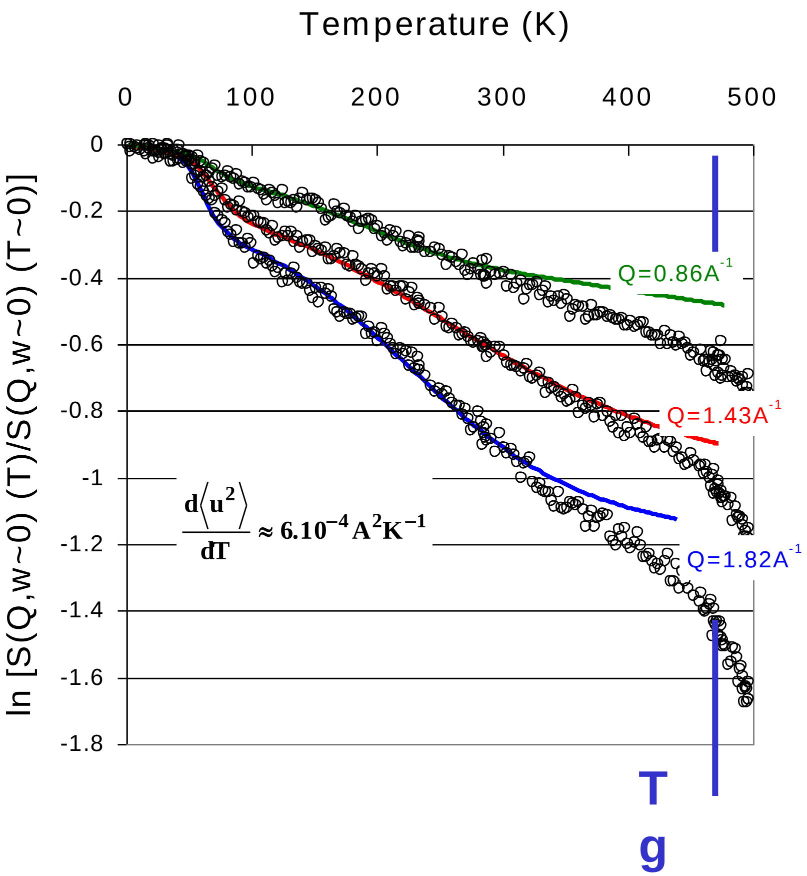
PARAMETERS

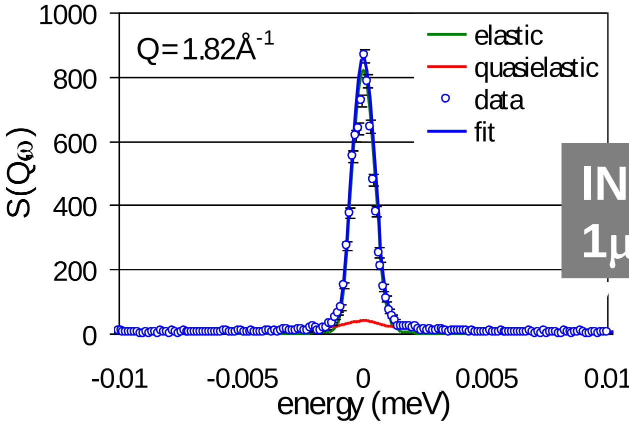
- <u2>(T) ← initial slope
- distribution: E$_A$ and σ
- Γo

ASSUMED

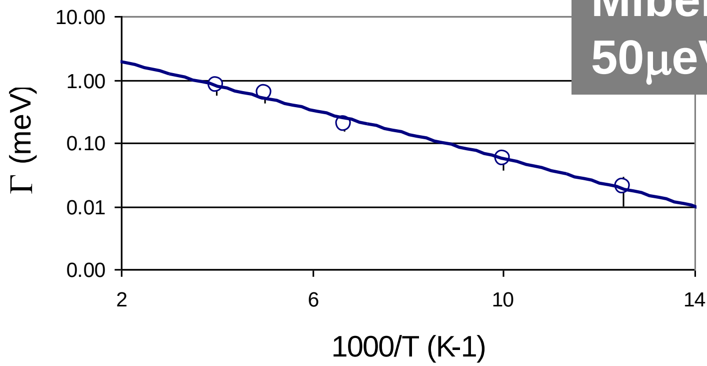
- geometry ← EISF
- activation ansatz: $\Gamma=\Gamma_0 e^{-\frac{E_A}{RT}}$

TMPC





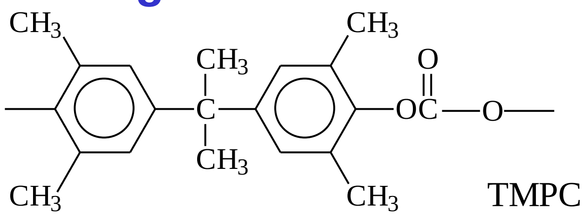
IN10
1μe



Mibemol
50μeV

Ea1~6
kJ/mol σ1~1

Ea2=15
kJ/mol σ1~5



TMPC

low temperature relaxation

TMPC first relaxation step:

- **very low T → low Eo**
- **rather sharp → narrow**

→ candidate: rotational tunneling

Mathiew equation: inelastic lines

$$S_{rot}(Q,\omega) = \frac{5+4jo(Qr)}{9}\delta(\omega) + \frac{2(1-jo(Qr))}{9}\left[\delta(\omega-\omega_t)+\delta(\omega+\omega_t)\right]$$

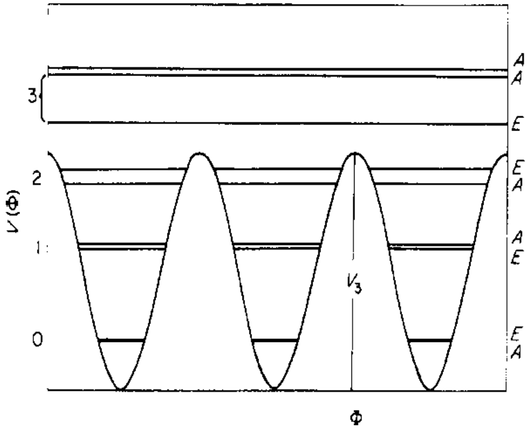
with $\hbar\omega_t \propto E_A{}^{3/4} e^{-\sqrt{E_A}}$

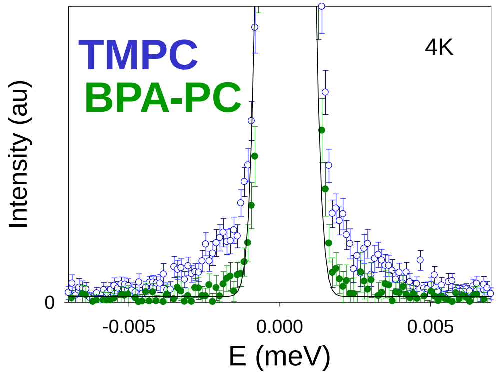
Distribution of EA →

highly asymmetric distribution of ω_t

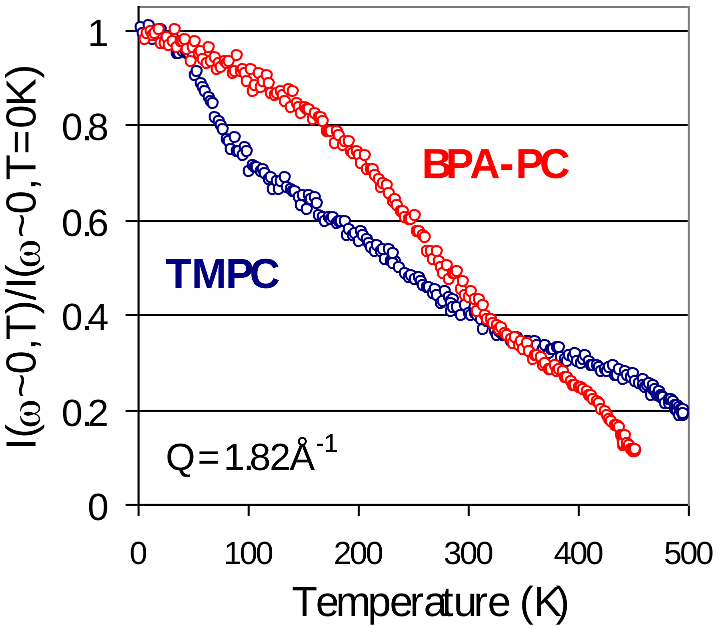
(Colmenero et al, PRL 1998)

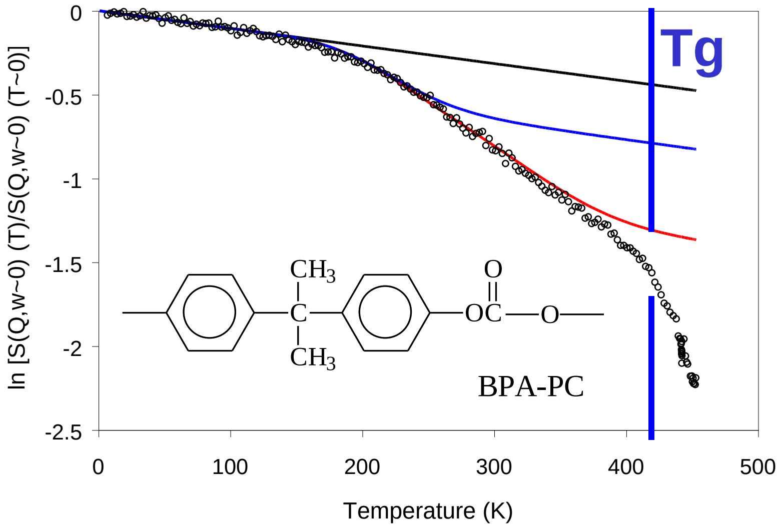
3-fold CH3 potential

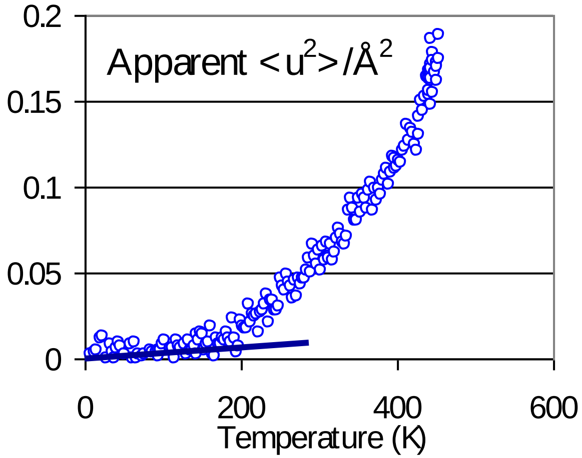




BPA-PC







Ephenyl~37 kJ/mol σ1~6

Ech3=15 kJ/mol σ1~3

compatible with TMPC

(after Spiess et al. 1987)

Distribution?

Glassy polymers:

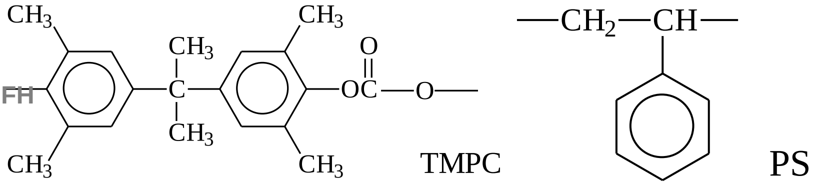
- backbone chain conformation
- Structural disorder

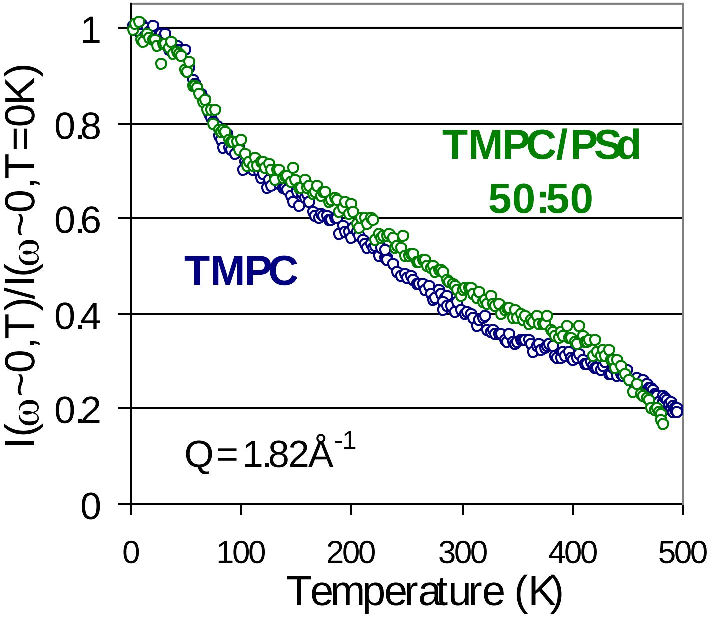
→

Blending

≠ inter-
≈ intra-
molecular potential.

TMPC: only PC miscible with PS, large χ_{FH}





1st step: no resolvable perturbation

2nd step: broadened distribution

intramolecular environment

- average E_A
- architectural considerations

intermolecular → limited effect on σ

Conclusions: CASE STUDY

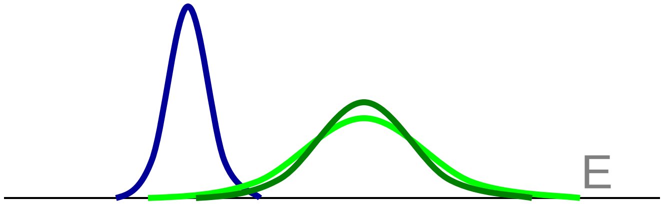
Characterisation local dynamics of PCs:

two architectures → toughest (BPA-PC) & most brittle (TMPC)

Technique combined backscattering window scans, inelastic BS & TOF

TMPC exhibits two methyl relaxations of rather different distribution of potentials

Blending affects $\sigma(E_A)$



BPA-PC Phenyl + methyl