Imperial College London

Neutrons in soft matter

Lecture 2 – Reflectometry & Dynamics

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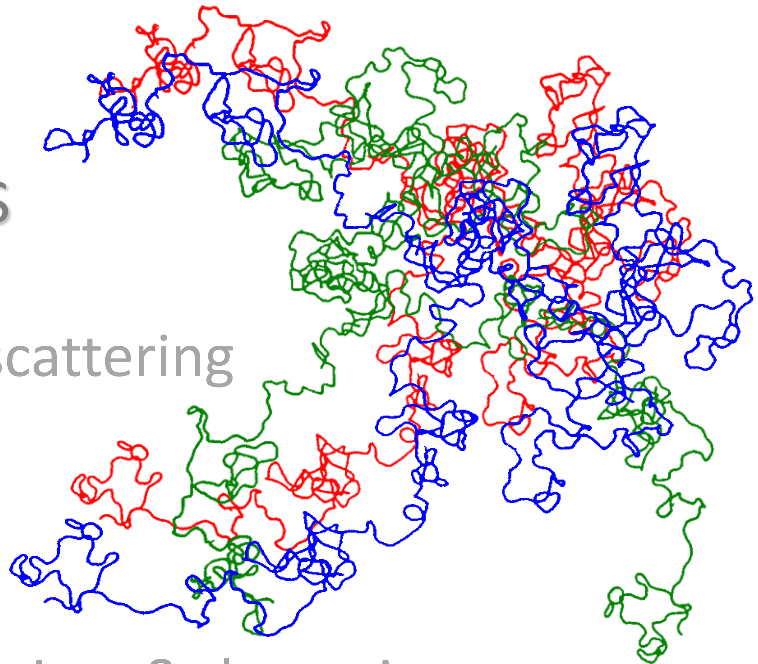
14th Oxford School on Neutron Scattering, 17 September 2015

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)

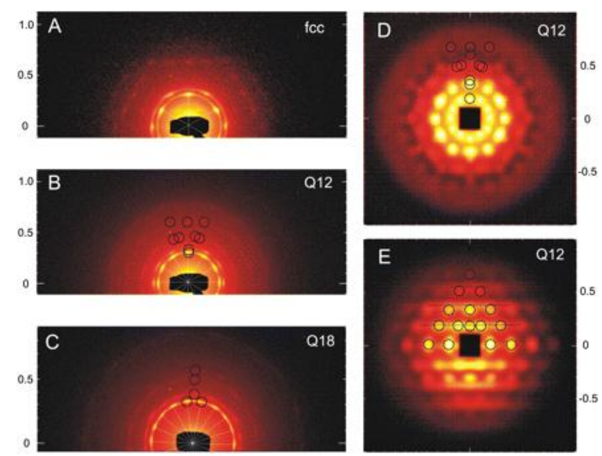
Polymer blends: interactions, conformation & dynamics

(equilibrium and phase separation)

Lecture 2 – Interfaces and dynamics

Reflectivity and diffusion

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

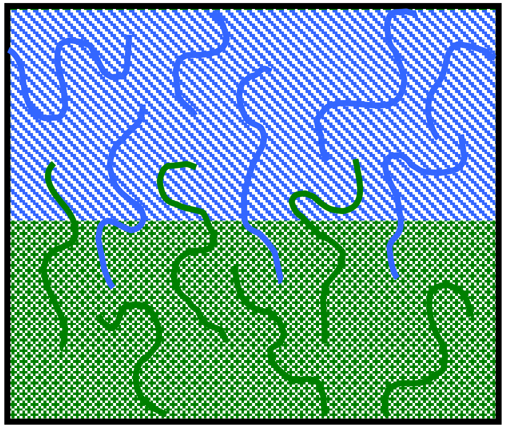


Forster et al (2011)

Reflectometry: study of interfaces

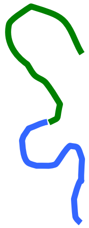
Miscible systems

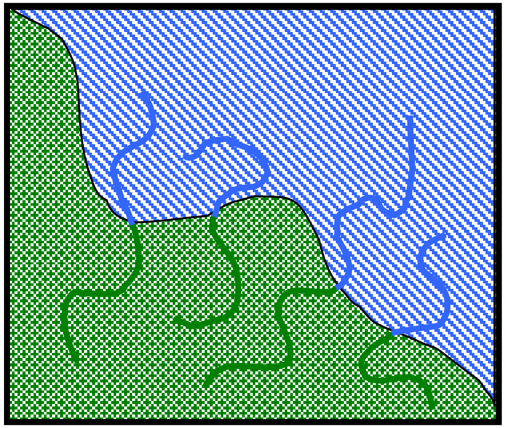
- Interdiffusion, e.g., welding



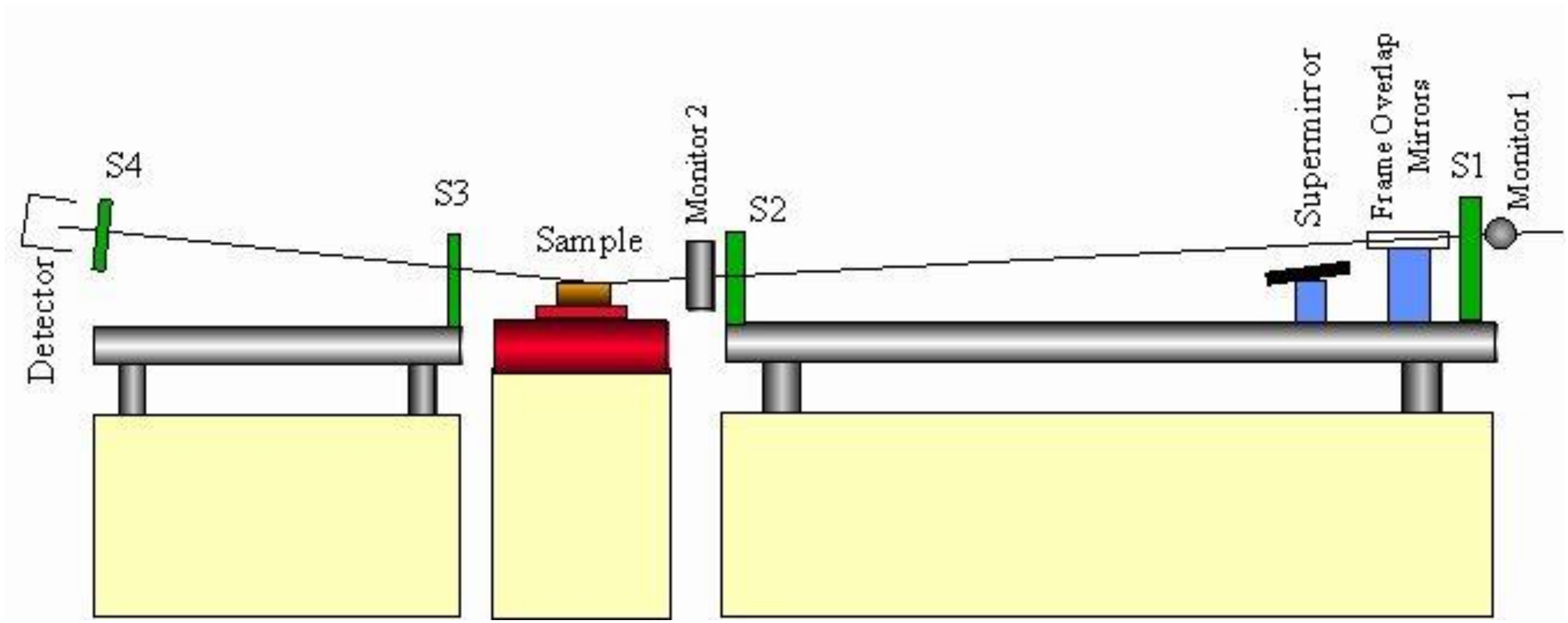
Immiscible systems

- 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)

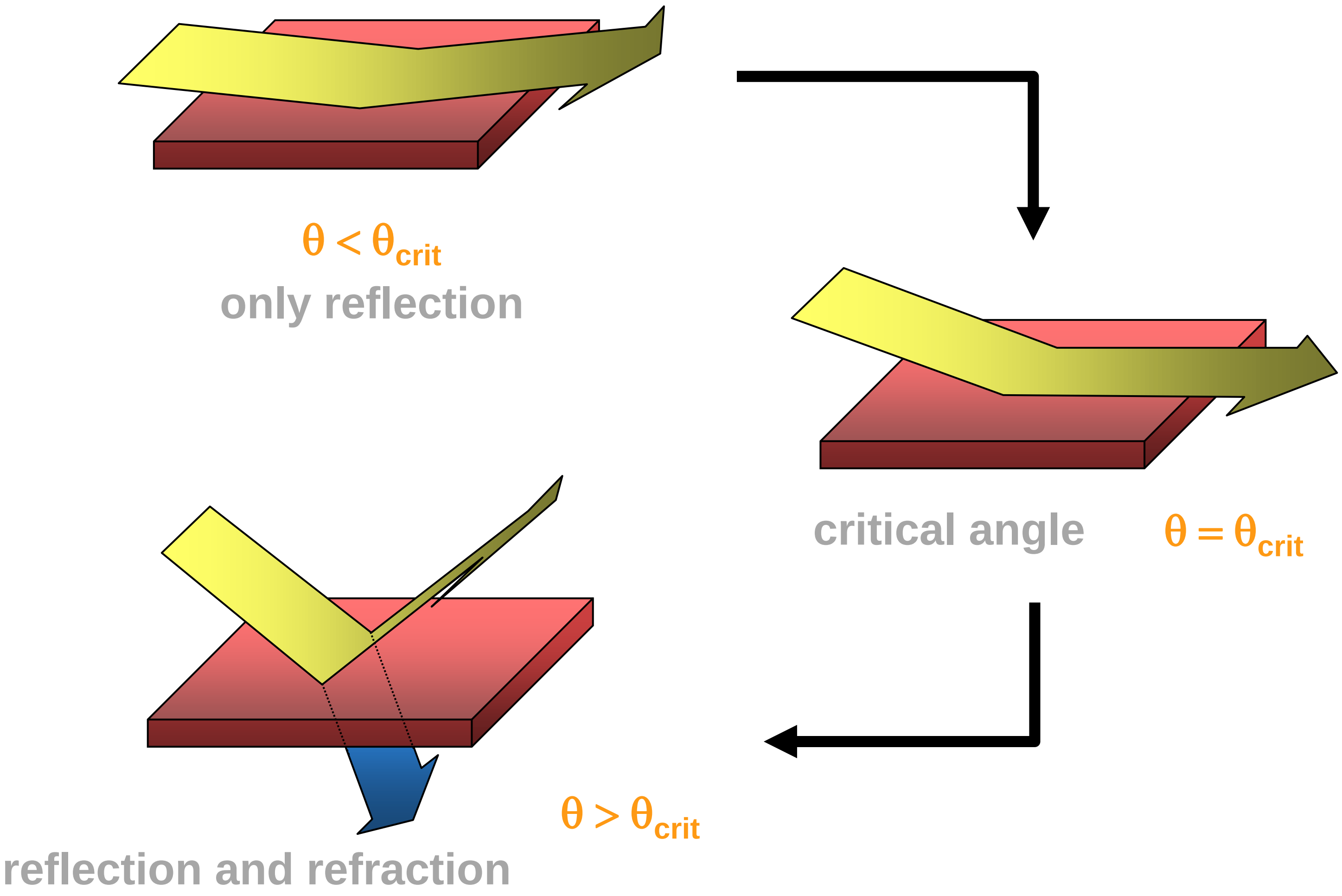
- Finite molecular weight limit

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

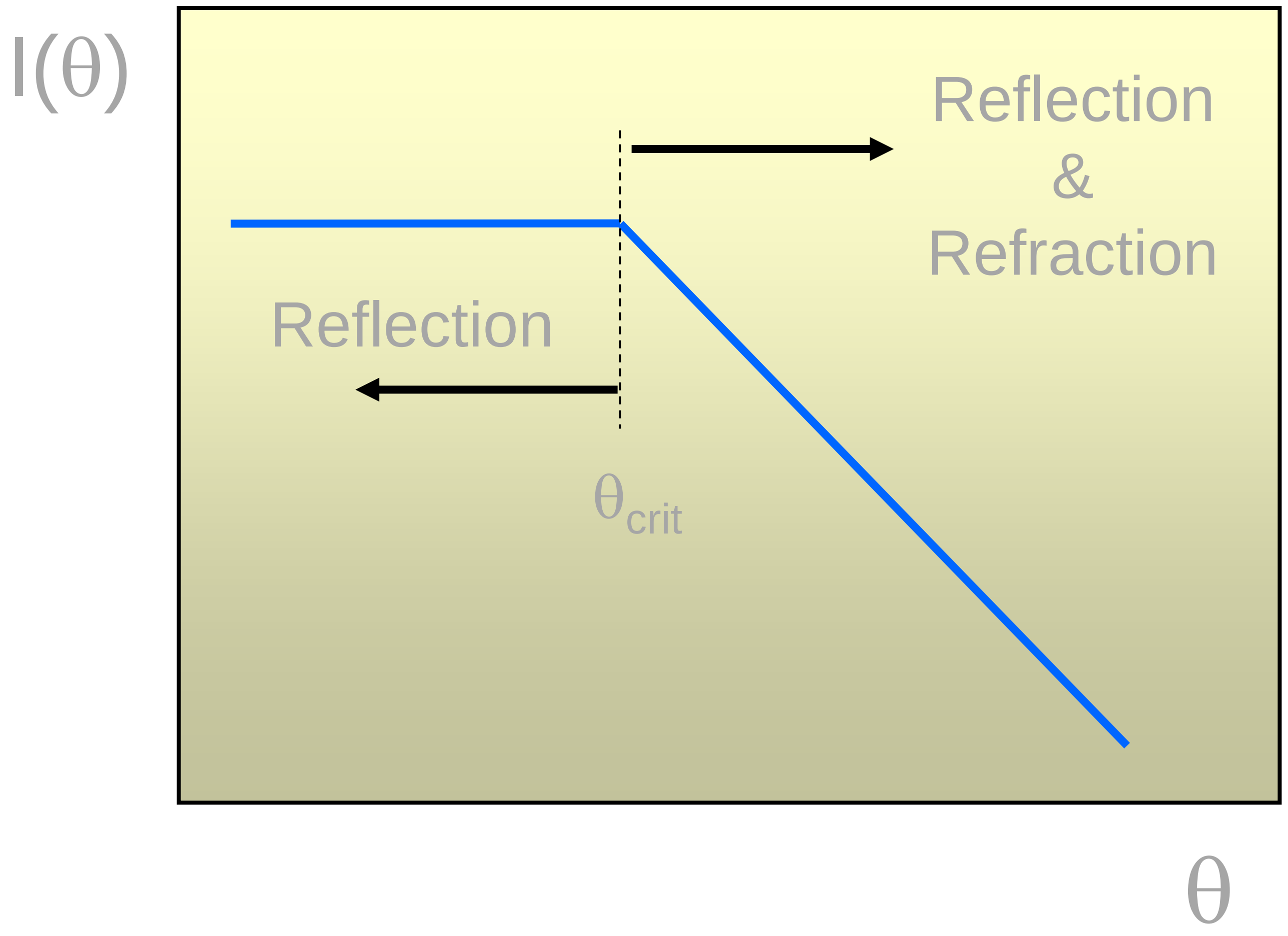
M Stamm & DW Schubert
Ann Rev Mater Sci
25 (1995) 325

$\Longrightarrow$ Measure interfacial width to find χ

Basics of Reflectivity

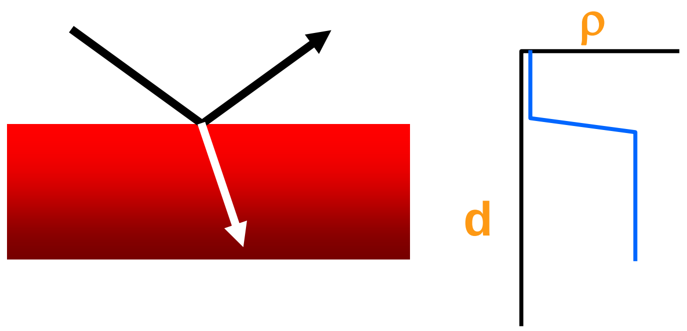


The Reflectivity Profile

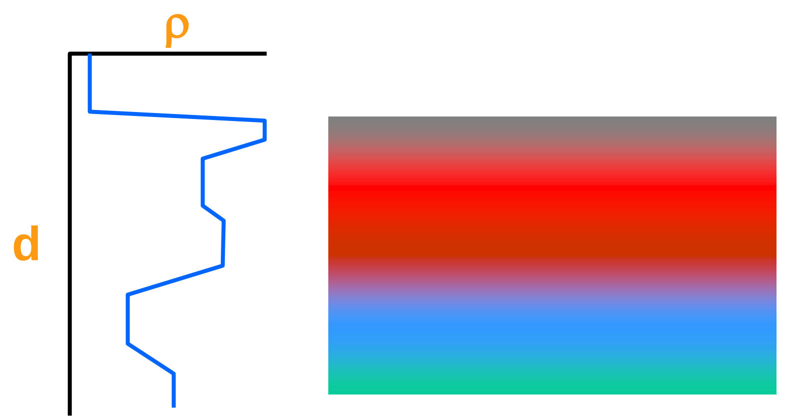


Information Content

Simplest Case



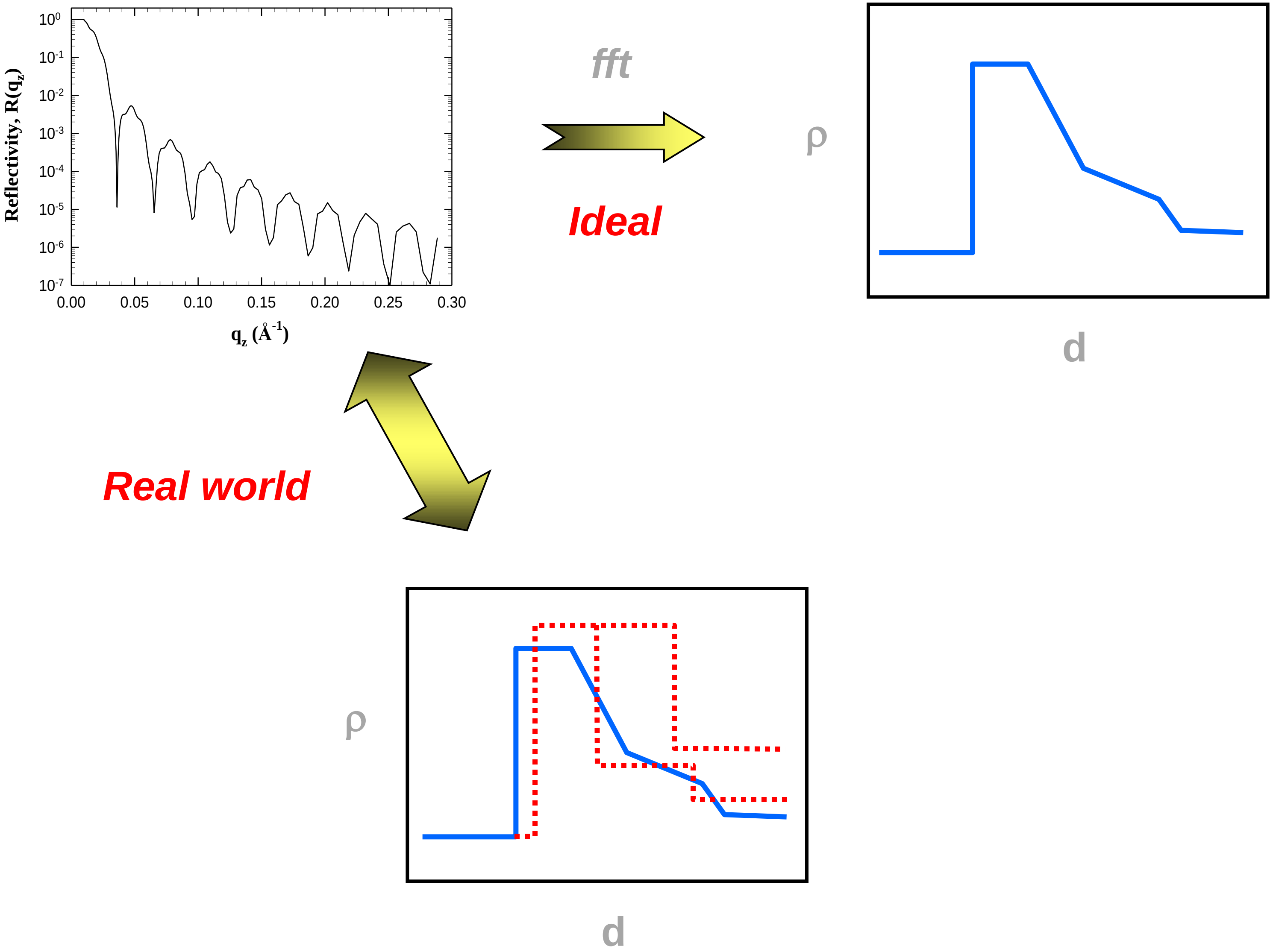
Complex Case



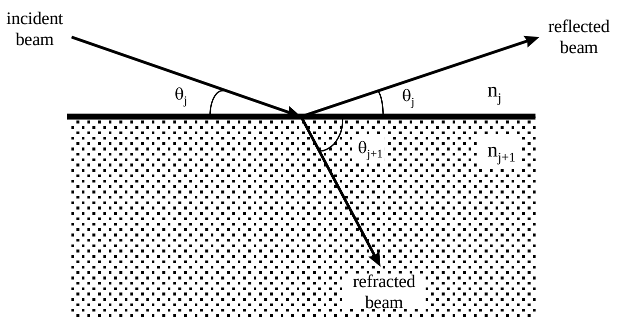
What about lateral information?

Off-specular !

Evaluating Reflectivity Data



Single layers and bilayers



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

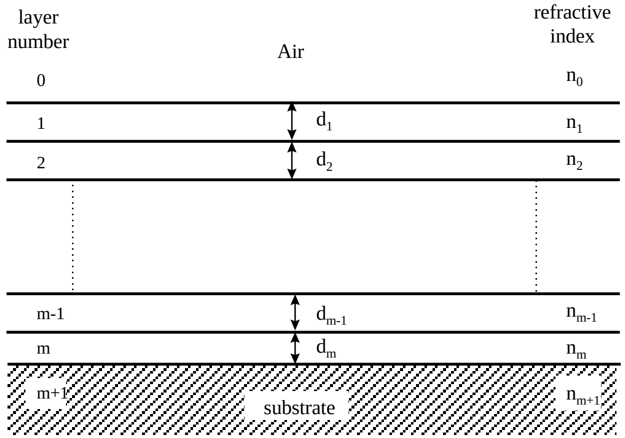
$$n_j \cos\theta_j = n_{j+1} \cos\theta_{j+1}$$ **Snell's Law**

$$r_{j,j+1} = \frac{n_j \sin\theta - n_{j+1} \sin\theta_{j+1}}{n_j \sin\theta + n_{j+1} \sin\theta_{j+1}}$$ **Fresnel's law**

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

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

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



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

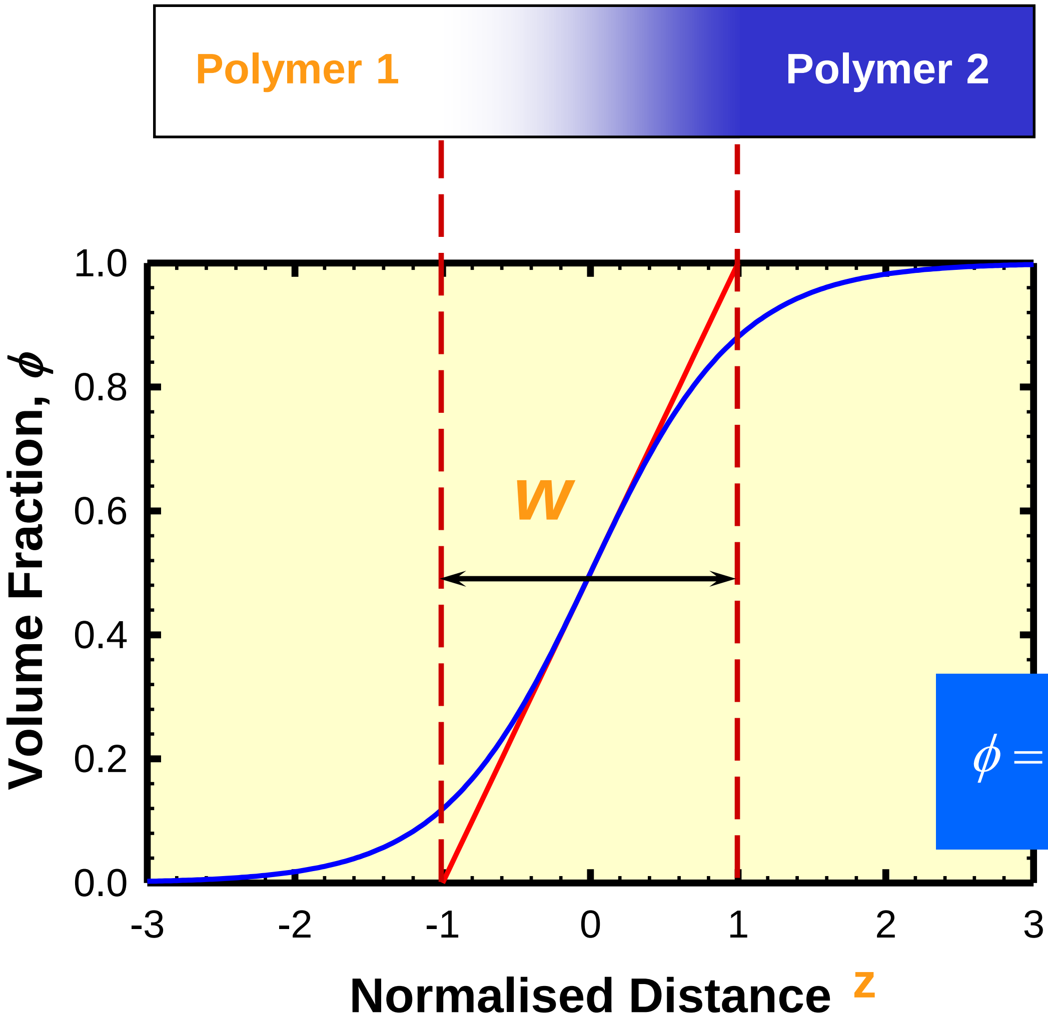
$$\beta_m = (2\pi/\lambda) n_m d_m \sin\theta$$

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

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

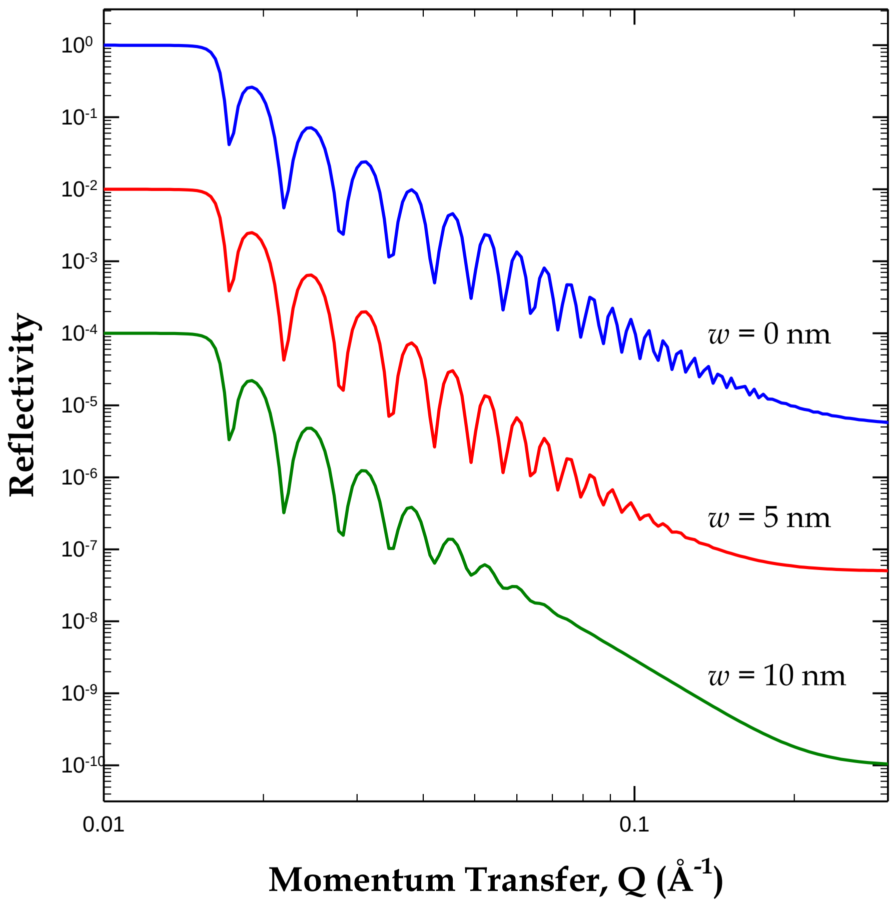
$$R = \left| \frac{(M_{11} + M_{12}\kappa_{m+1})\kappa_0 - (M_{21} + M_{22})\kappa_{m+1}}{(M_{11} + M_{12}\kappa_{m+1})\kappa_0 + (M_{21} + M_{22})\kappa_{m+1}} \right|^2$$

Interfacial Width - Definition

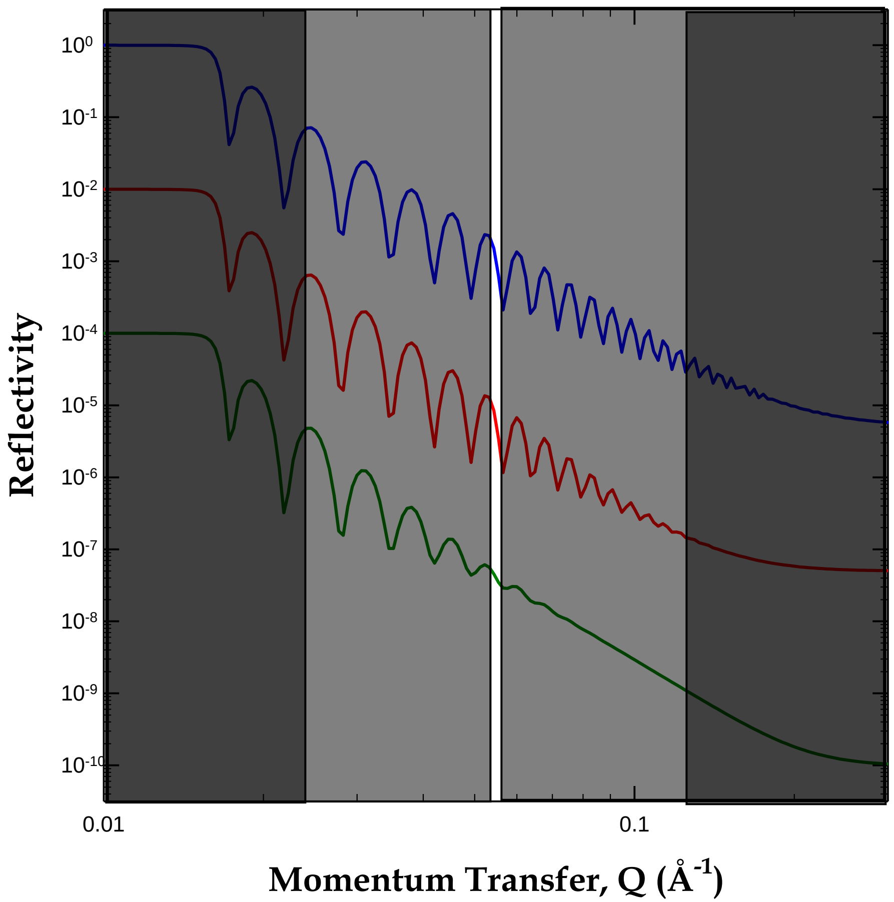


$$\phi = \frac{1}{2}\left(1 + \tanh\left(\frac{2z}{w}\right)\right)$$

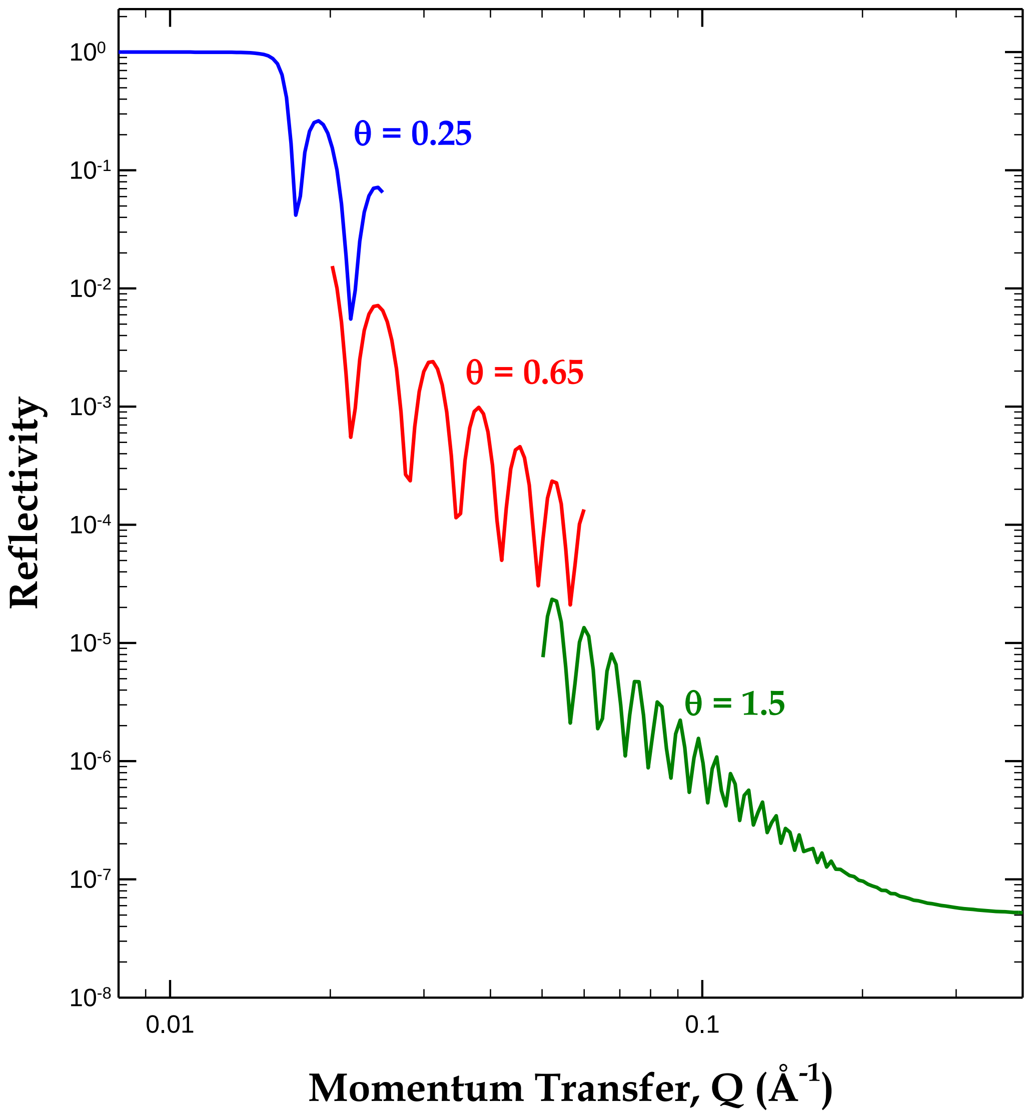
Effect of Interdiffusion on Reflectivity Profiles

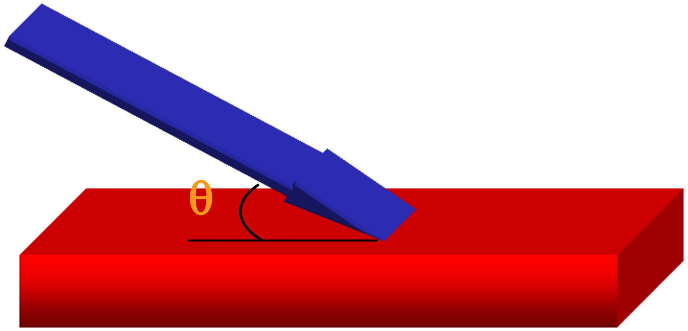


Effect of Limiting Q range on Observation Window



Effect of Angle on the Q Range

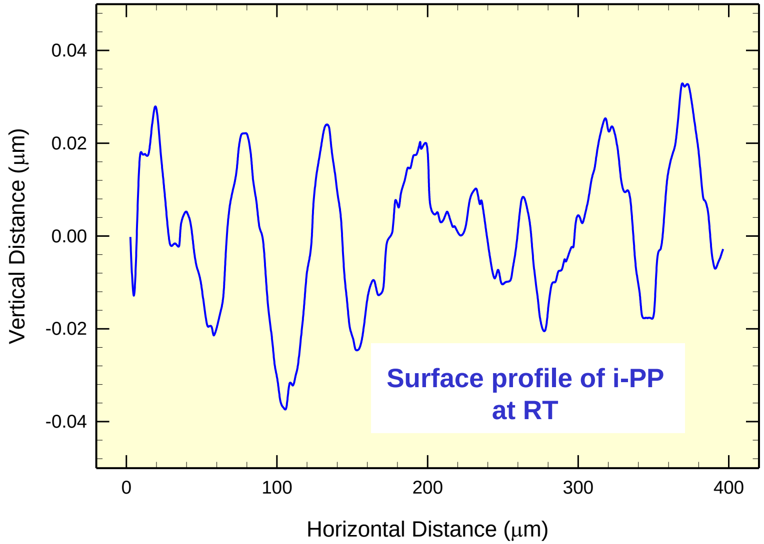


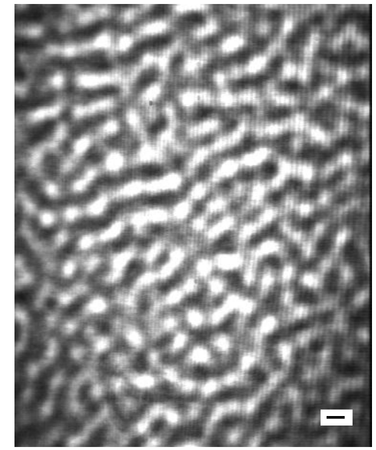


$$Q = \frac{4\pi}{\lambda}\sin\theta$$

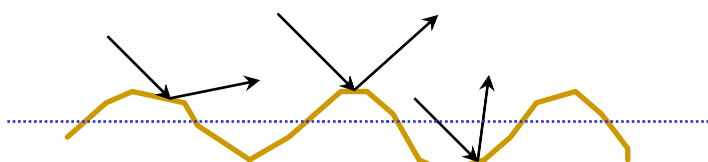
0.05 < λ (nm) < 0.65

Effect of Crystallinity on reflectivity

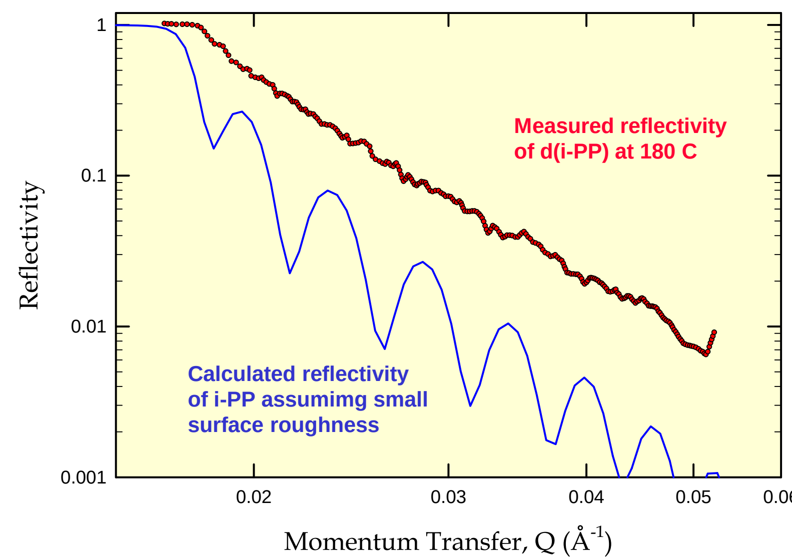




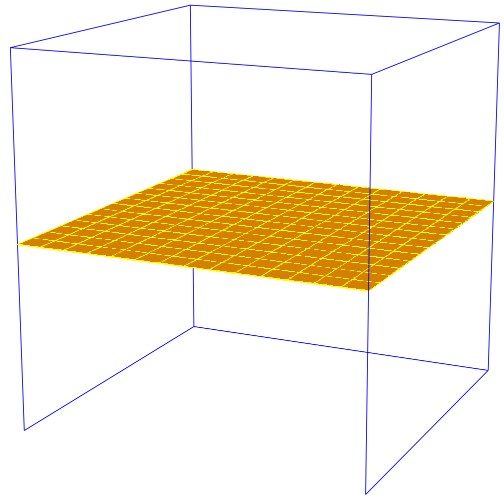
Brewster angle micrograph of surface of i-PP (bar 20μm)



Roughness causes off-specular scattering and increased resolution term.

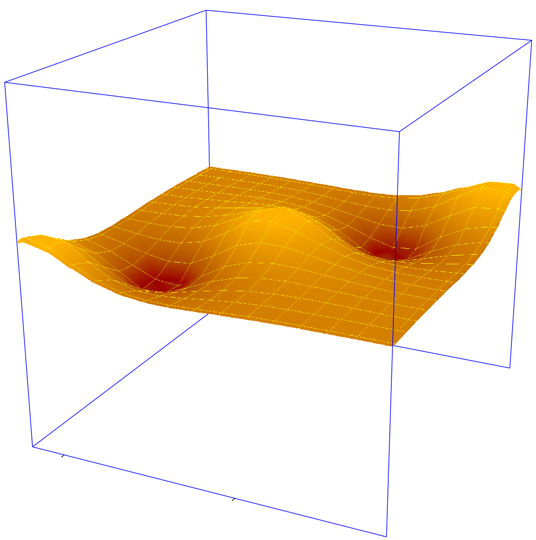


Thermally Excited Capillary Waves

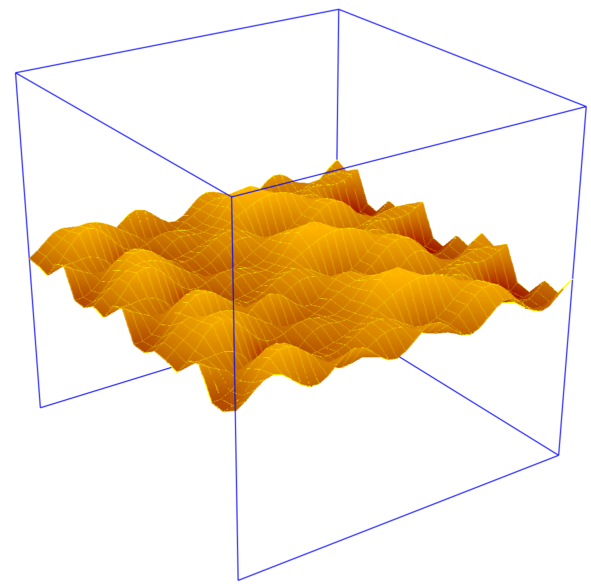


Mean field theory assumes that the interface is flat.

At equilibrium capillary waves are thermally excited.

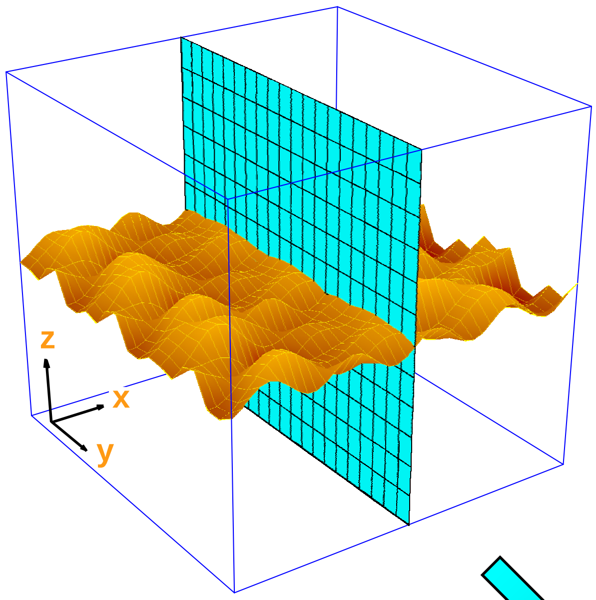


According to the equipartition theorem each mode increases the surface energy by 0.5 kT.



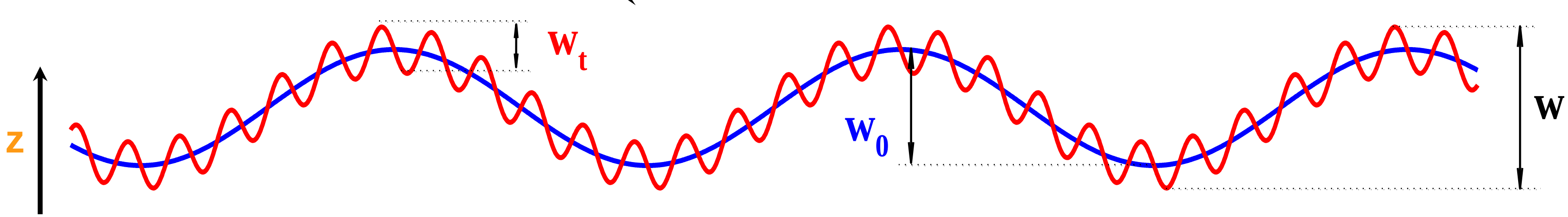
The actual surface is roughened by a superposition of all possible capillary wave modes.

NR Measured Interfacial Width



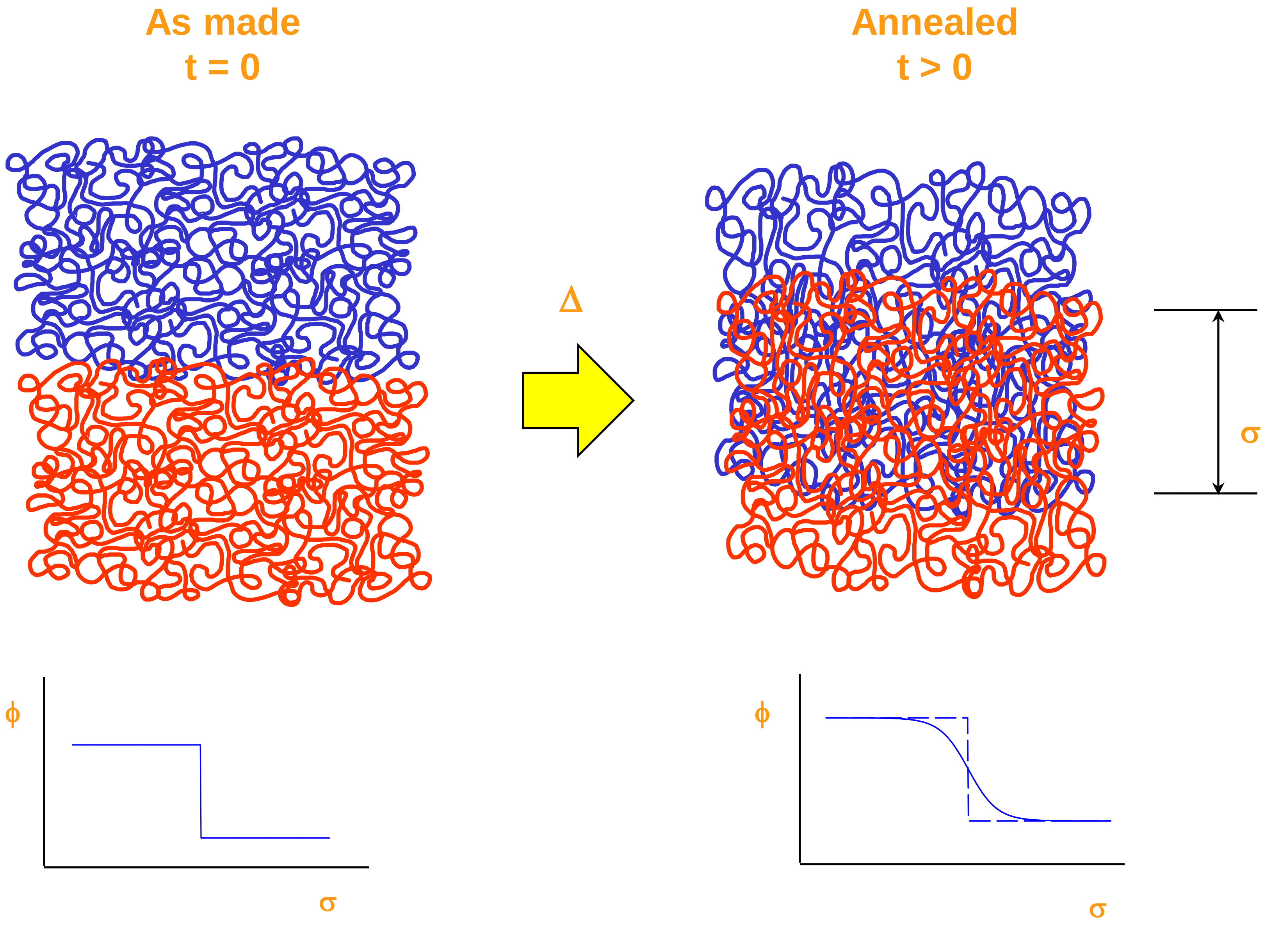
$$w = (w_t^2 + w_0^2)^{0.5}$$

Definition of w_0 dominates derivation of w_t



Projection onto z-y plan

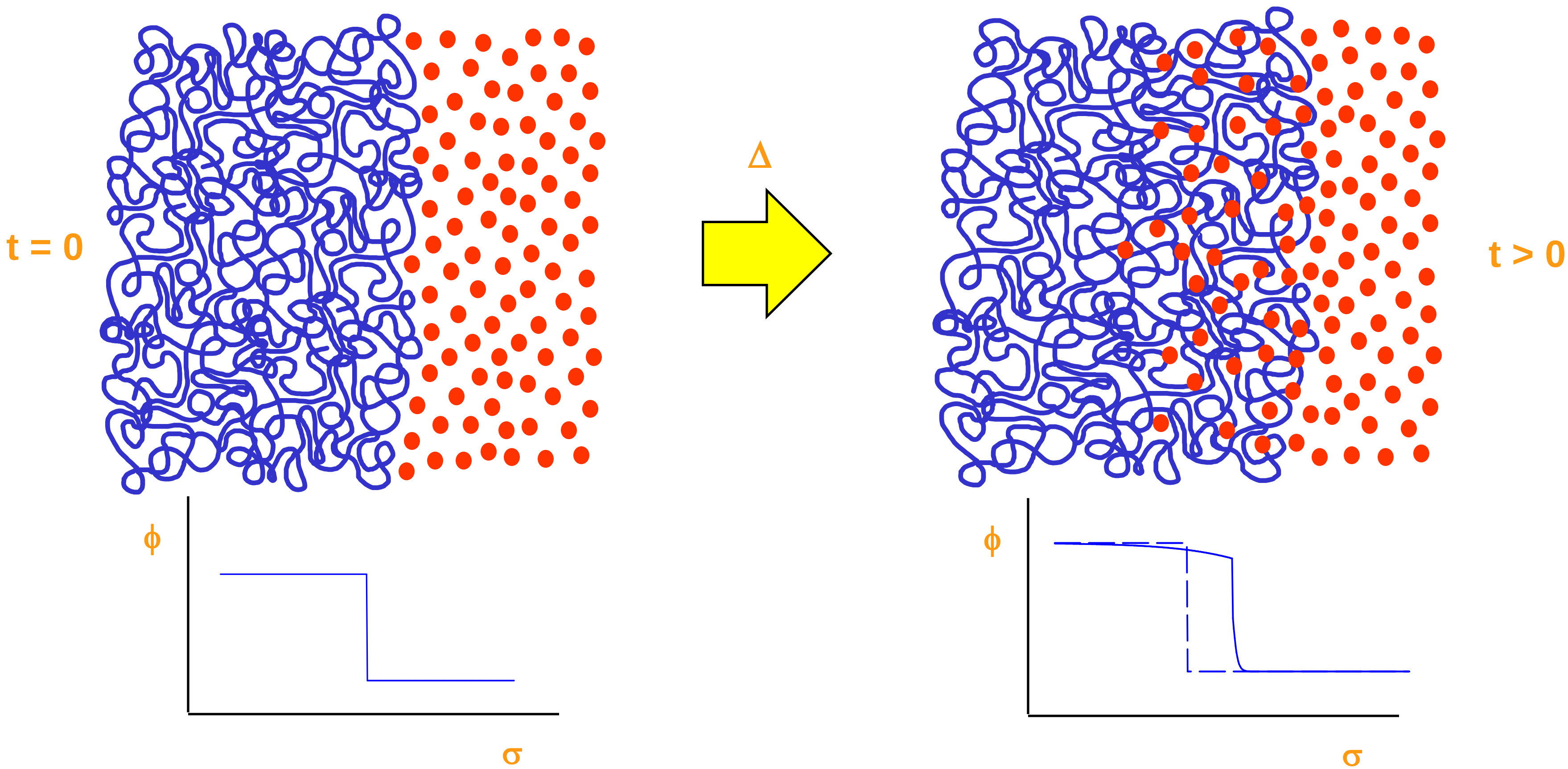
Polymer Interdiffusion



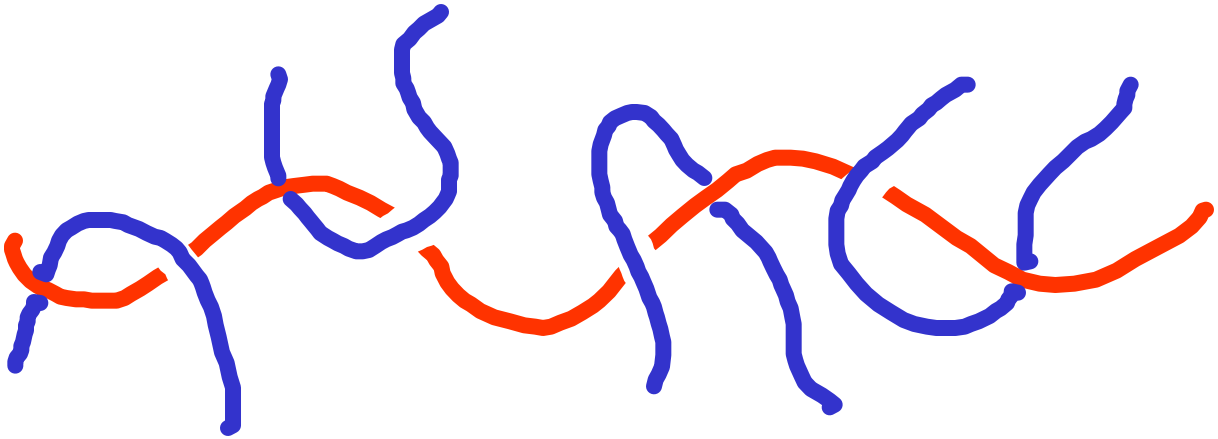
Non-Fickian Diffusion - Case II Diffusion

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

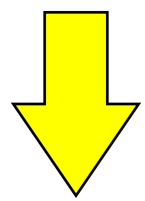
Non-Fickian Diffusion



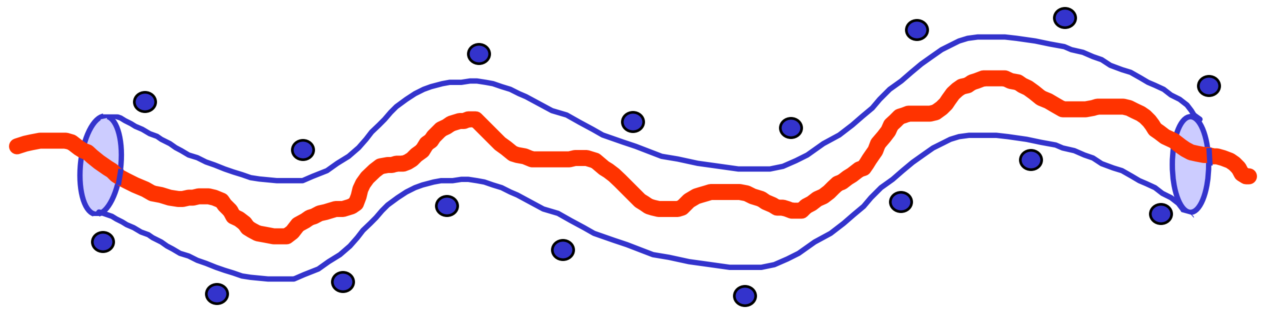
The Tube Model



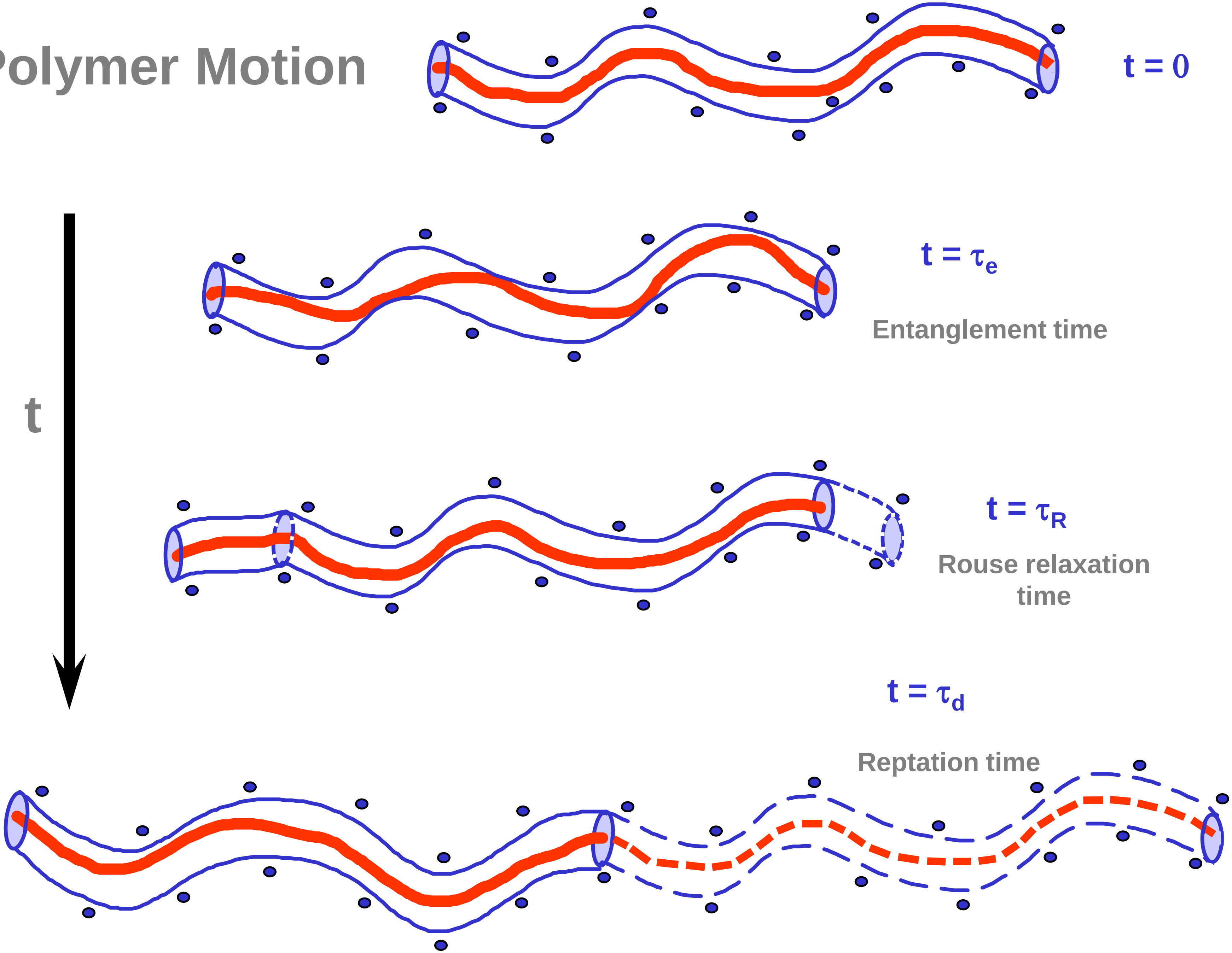
Polymer chains in the melt



Each chain can be considered to be constrained within a tube



Polymer Motion



Polymer Diffusion

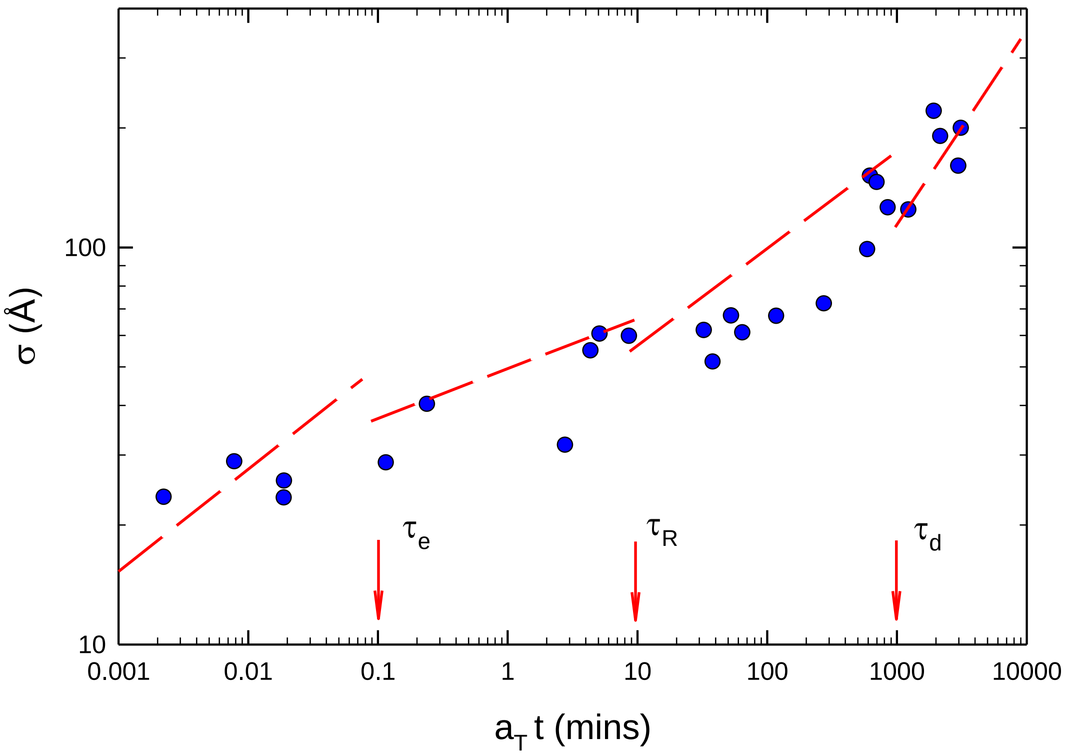
$t < \tau_e$ ⇨ $\sigma \propto t^{1/4}$

$\tau_e < t < \tau_R$ ⇨ $\sigma \propto t^{1/8}$

$\tau_R < t < \tau_d$ ⇨ $\sigma \propto t^{1/4}$

$t > \tau_d$ ⇨ $\sigma \propto t^{1/2}$

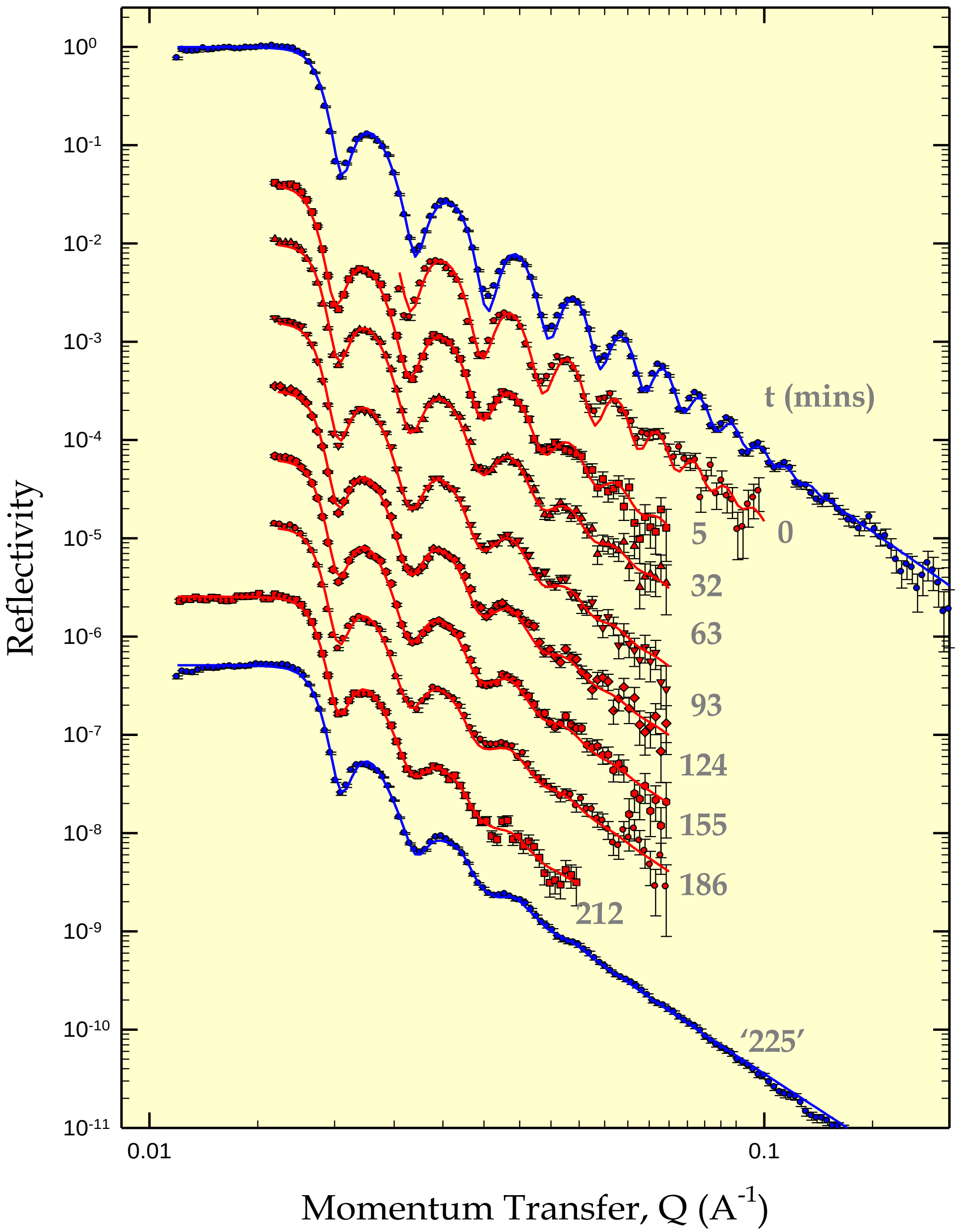
NR Results



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:

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

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

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:

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

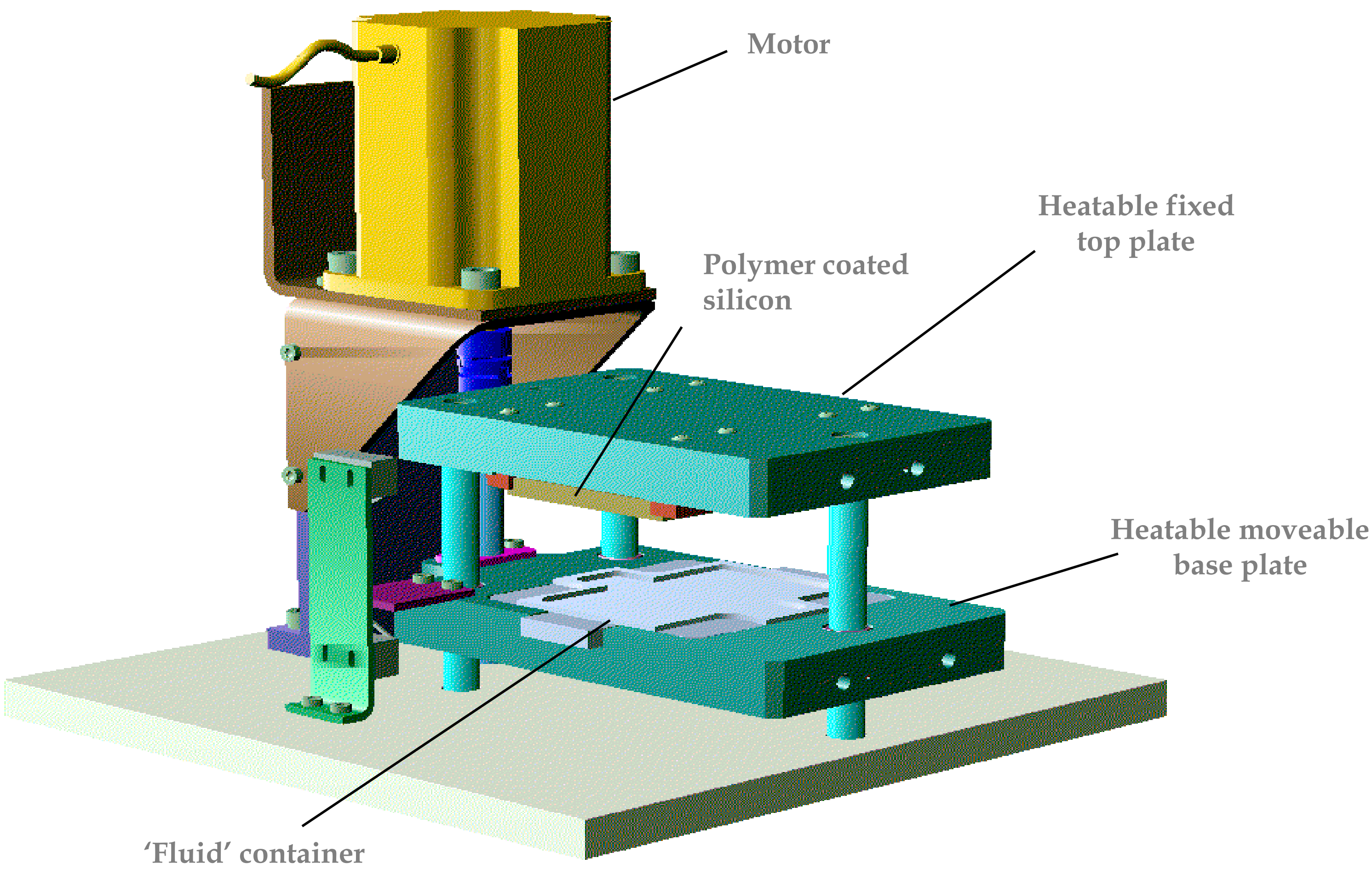
$$\tau_r = 3223 \pm 363\ \mathrm{s\ (dPS)}$$
$$= 4333 \pm 489\ \mathrm{s\ (hPS)}$$

Rouse time:

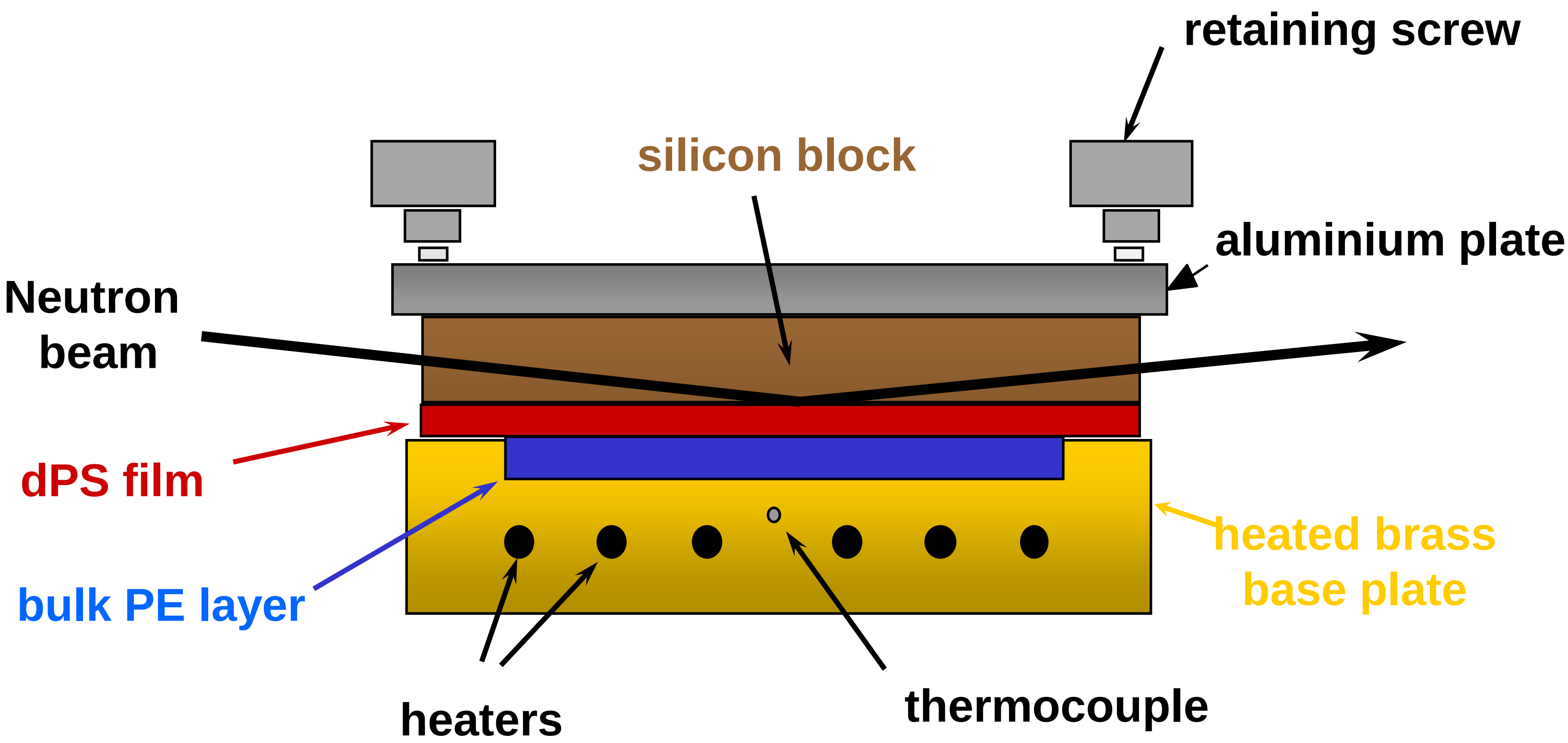
$$\tau_R = \frac{d_T^2}{9\pi^2 D}$$

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

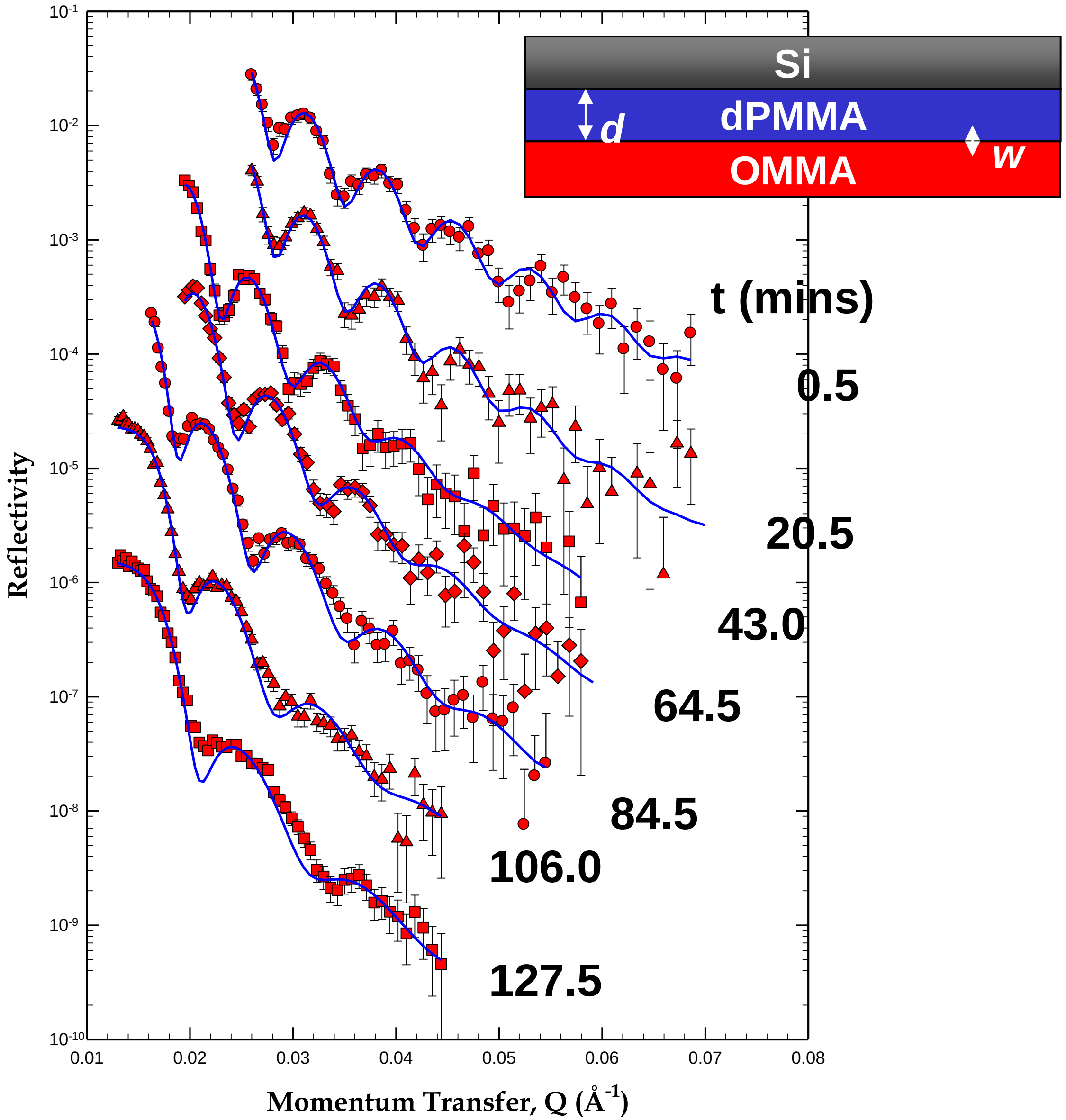
Polymer-Oligomer Interdiffusion Reflectivity Cell



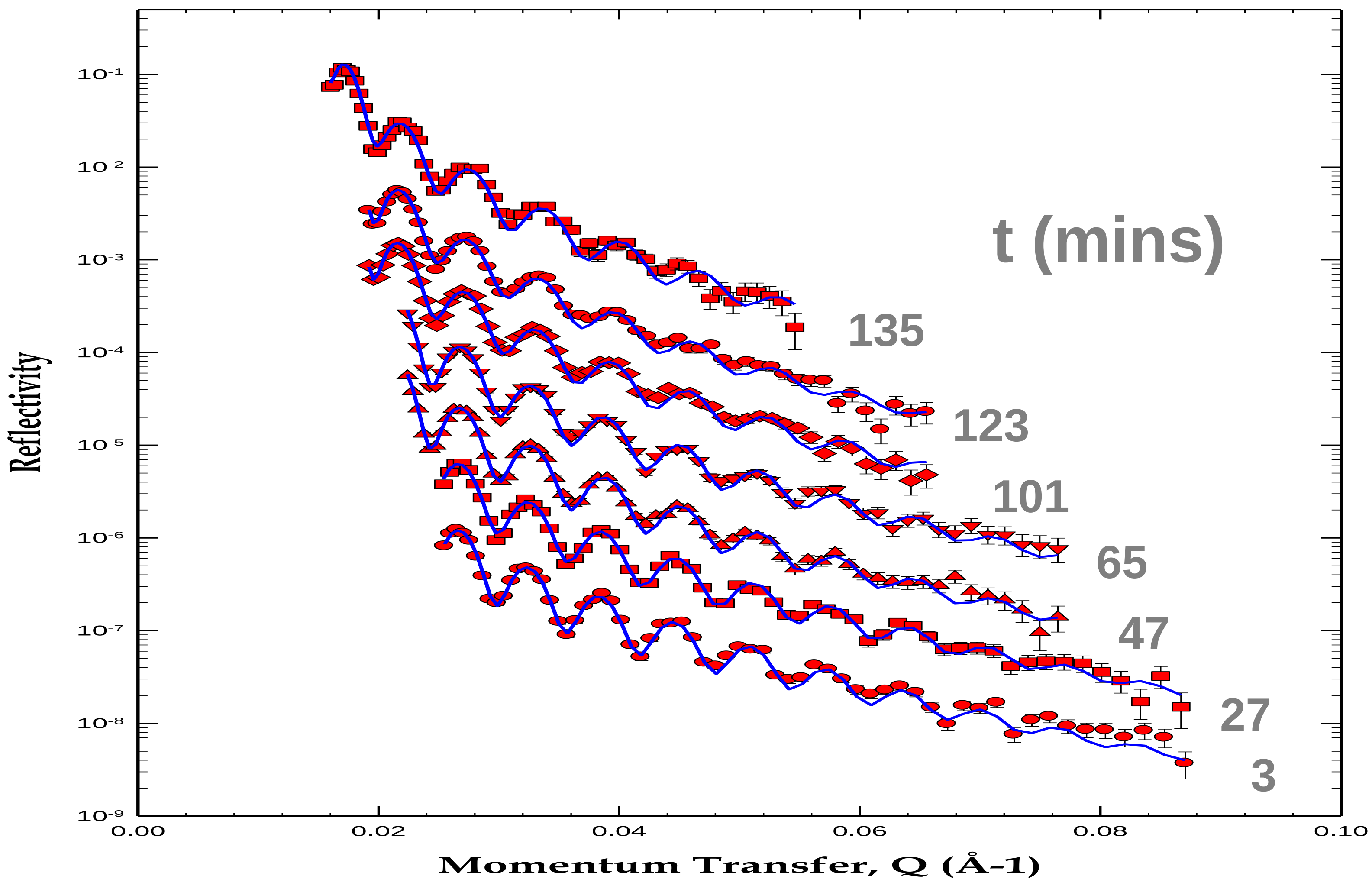
Neutron Reflectivity Melt Cell



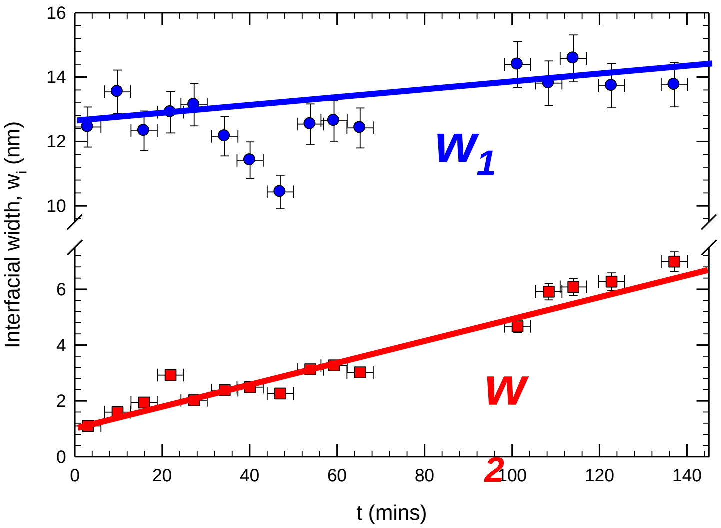
dPMMA(100k) / OMMA(510) @ 45 C

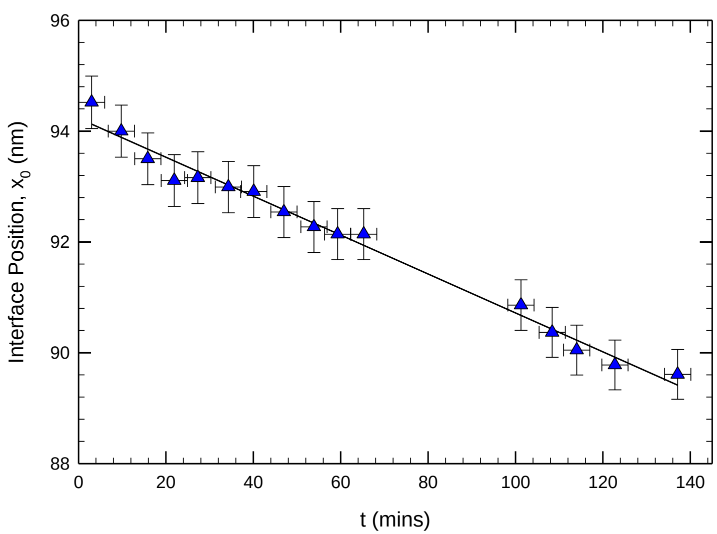


dPS (101k) / OSt (1100) Interdiffusion @ 65C

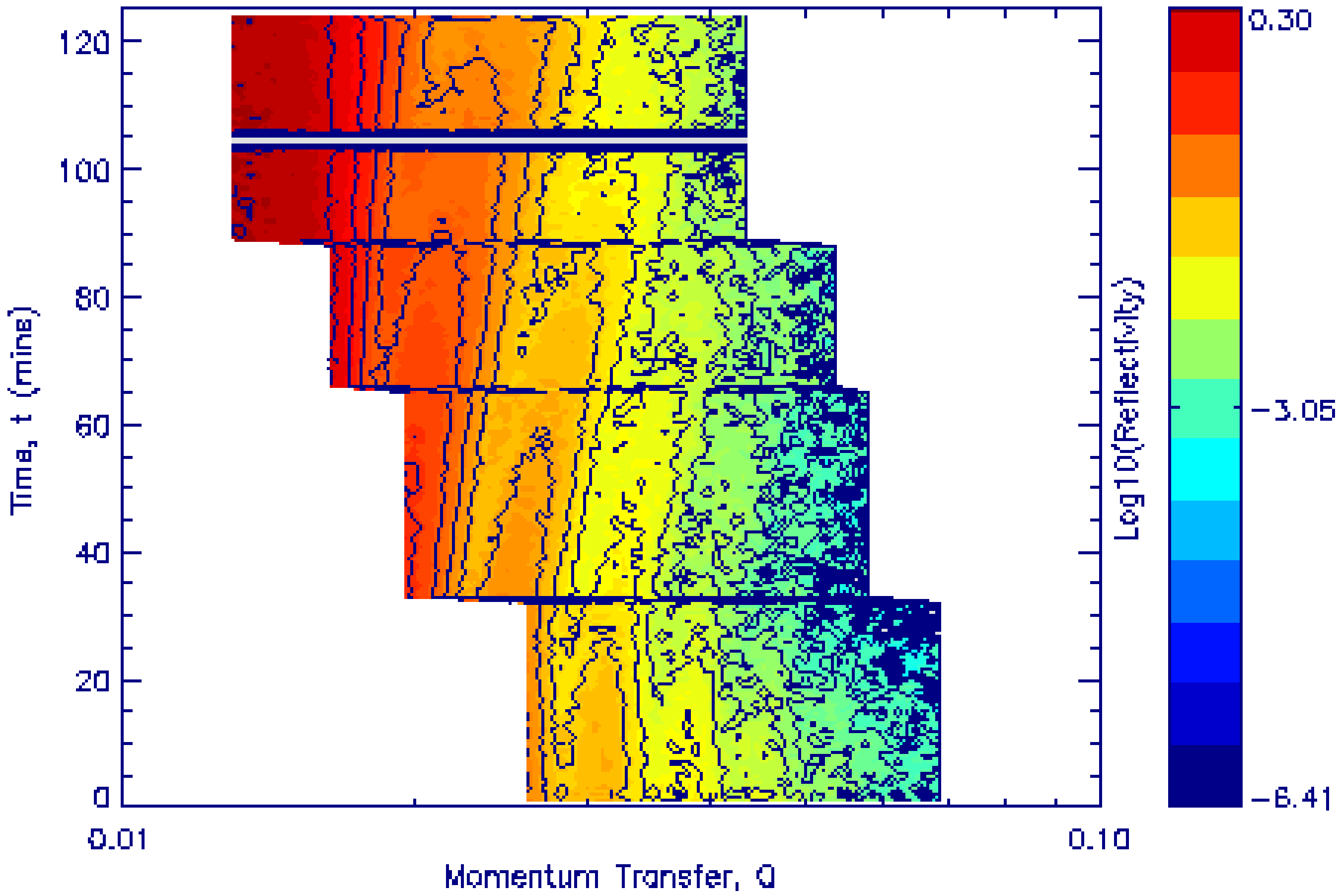


dPS (101k) / OSt (1100) Interdiffusion @ 65C

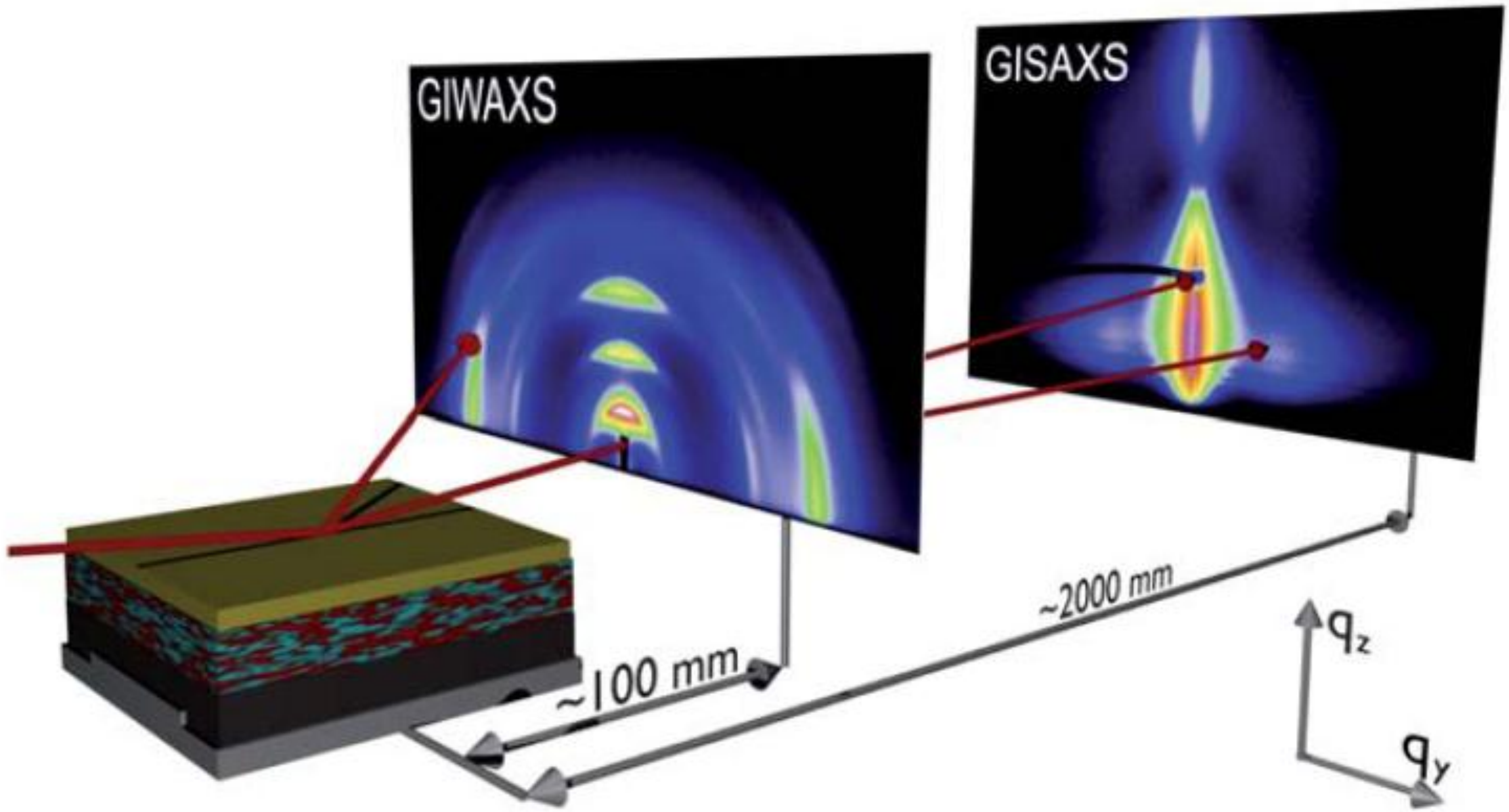




Off-specular reflection

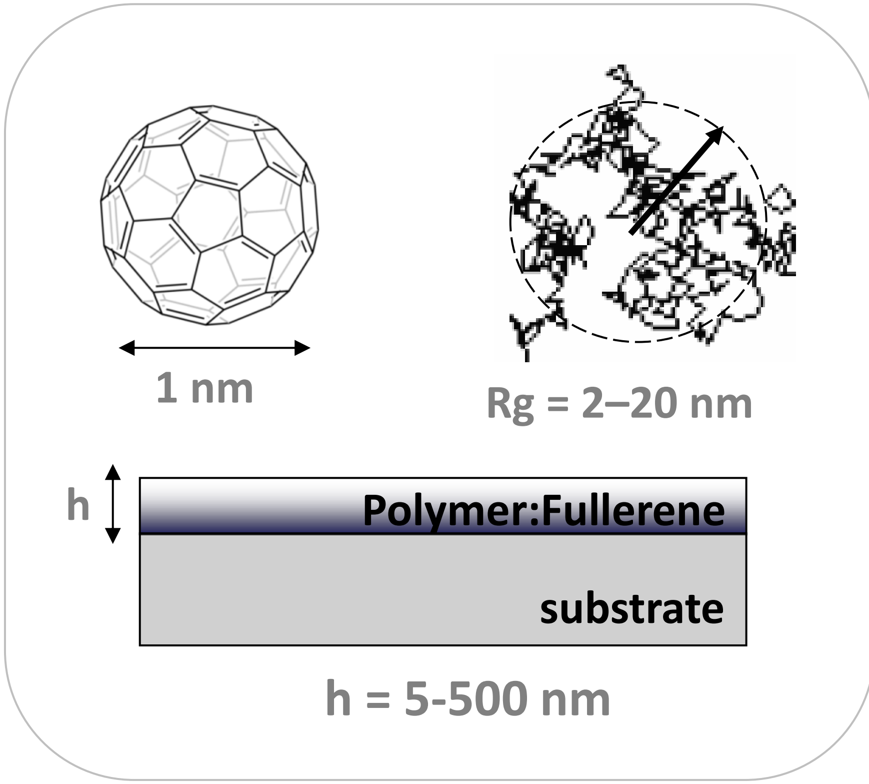


Grazing incidence: wide and small angle

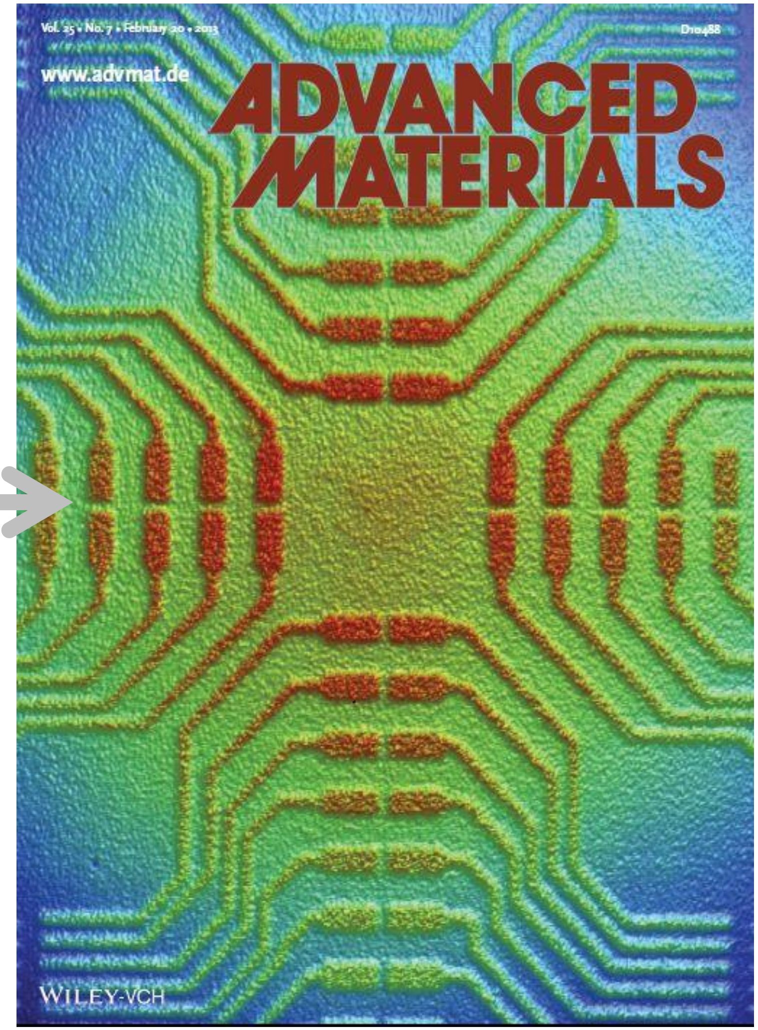


P Muller (2011)

Polymer-fullerene blends



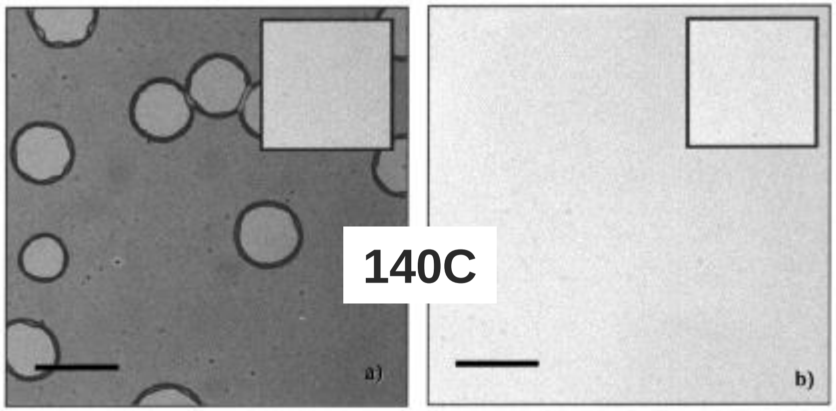
?

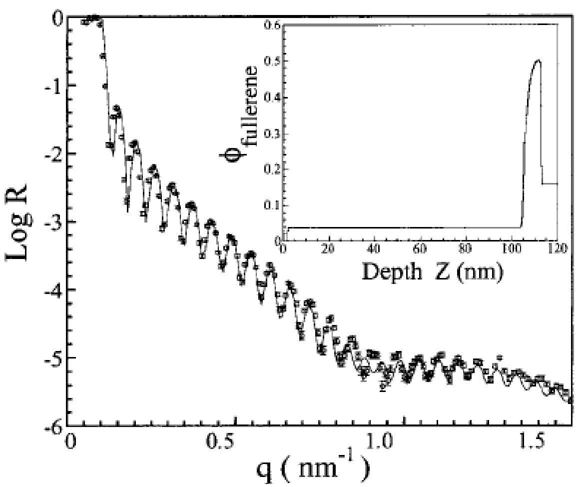


Adv. Mater. **25** 985-991 (2013)

Thin films

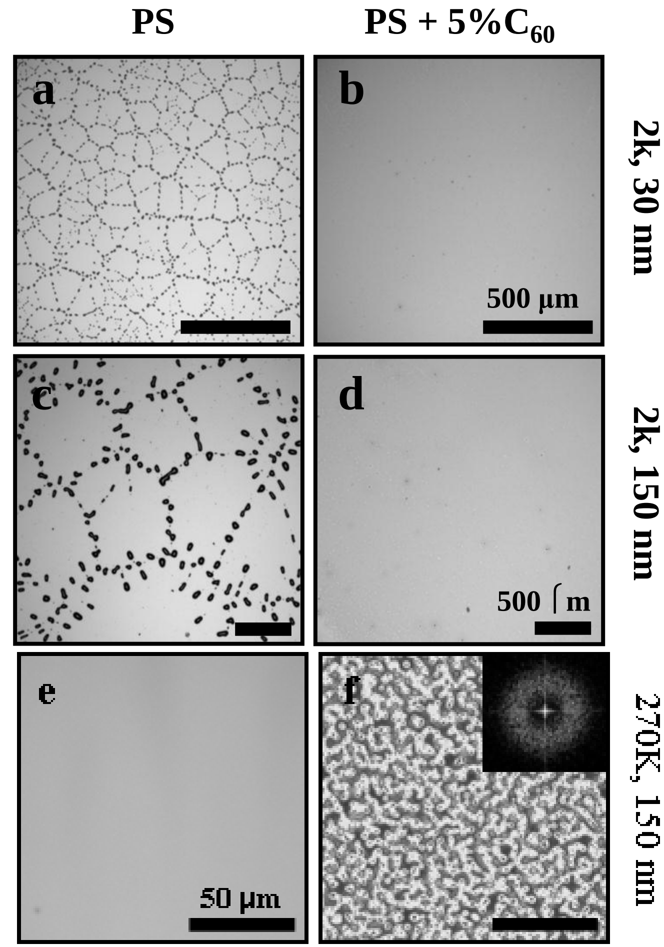
PS (2k), 30 nm　　　1% C60, 30 nm





PS+5% C60 h = 100nm

GISANS & reflectometry



140°C

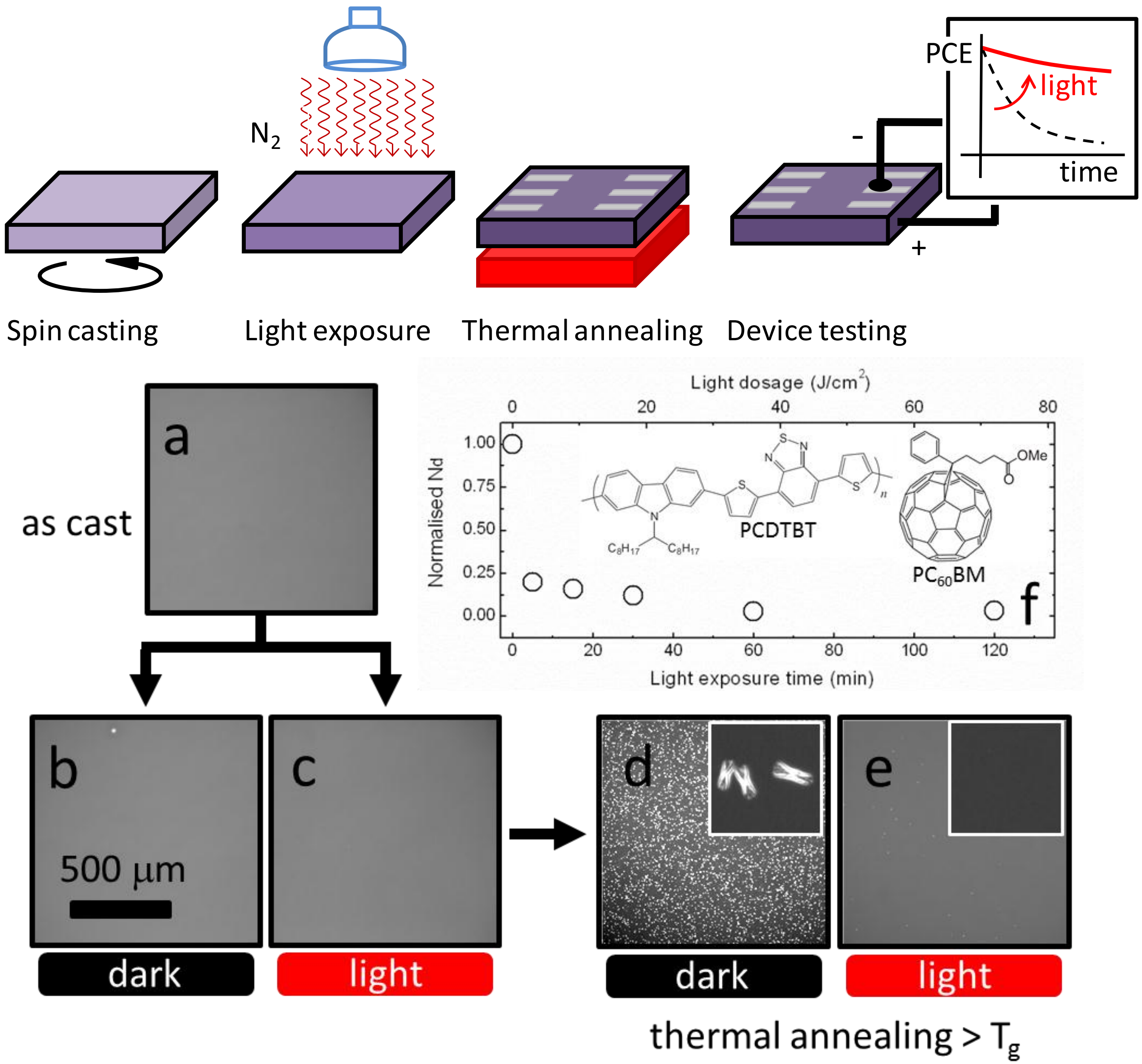
180°C

180°C

'Spinodal nucleation'

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

Organic Solar Cell lifetime?



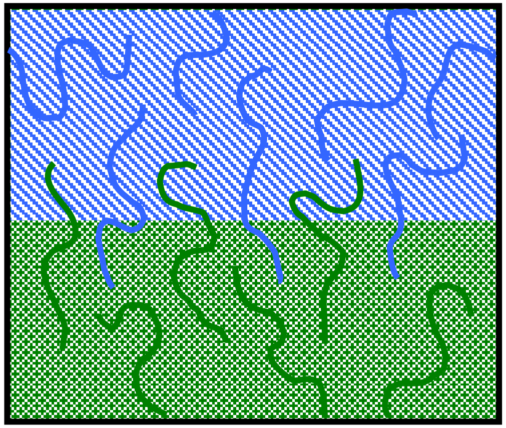
Angew. Chem. Int. Ed. 53, 12870-12875 (2014)

Nature Communications 4, 2227 (2013)

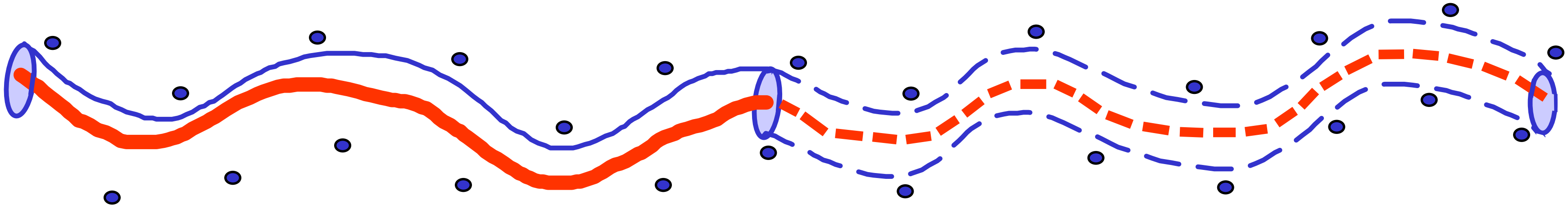
Summary

Reflectivity

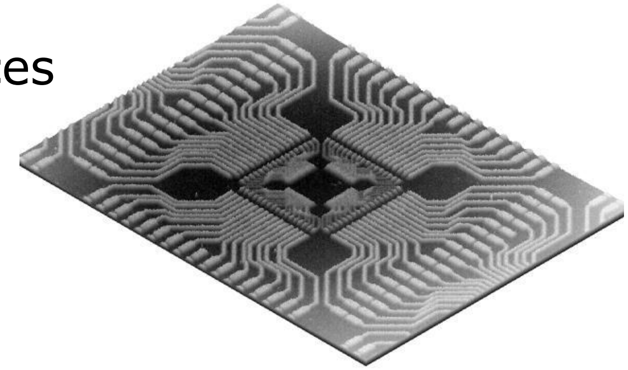
- study and design interfaces



- investigate diffusion mechanisms



- engineer 'functional' surfaces / devices



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Neutrons in soft matter

Lecture 2 (II) – Dynamics

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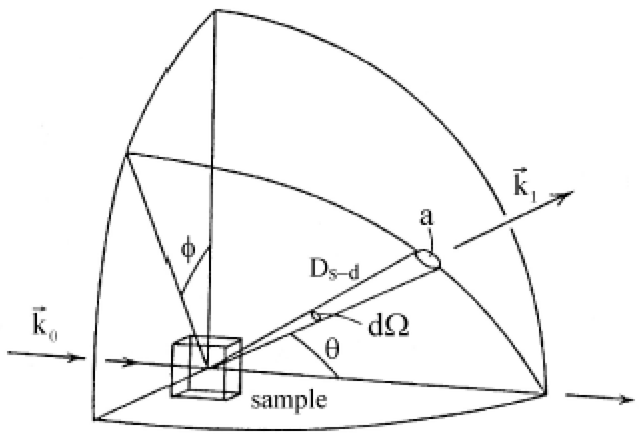
Scattering theory reminder



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)

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

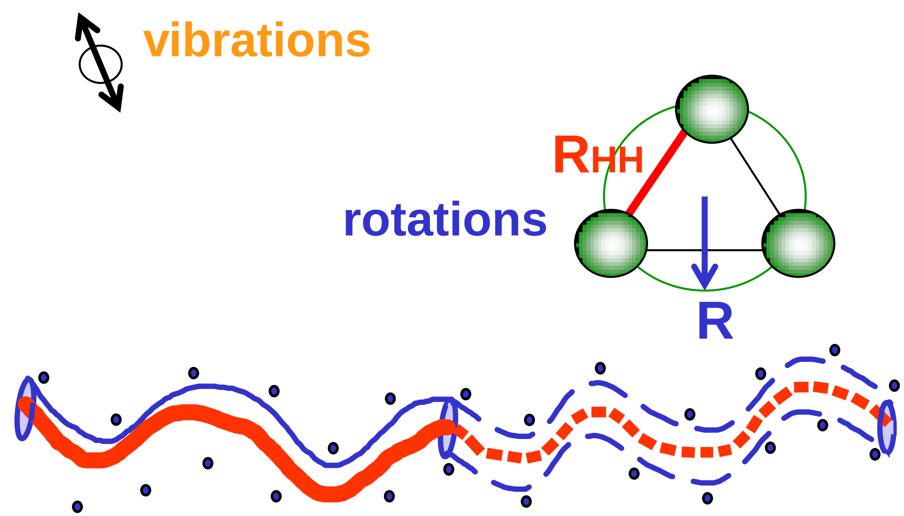
Intermediate scattering function

FT (r,q)

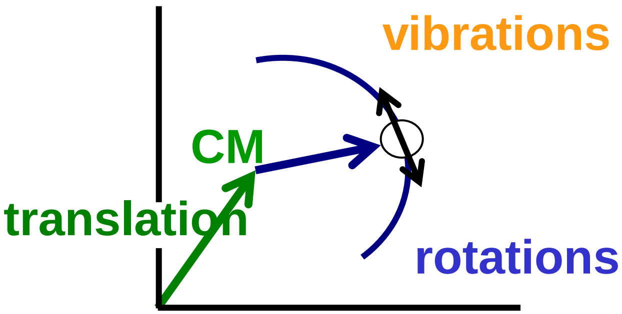
$$I_s(\mathbf{q},t) = \frac{1}{N}\sum_i\left\langle e^{-i\mathbf{q}\cdot\mathbf{R}_i(0)}e^{i\mathbf{q}\cdot\mathbf{R}_i(t)}\right\rangle e^{-i\omega t}.$$

Pair correlation function

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

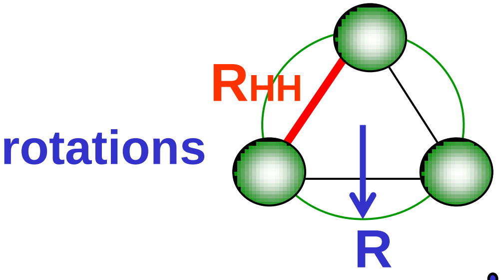


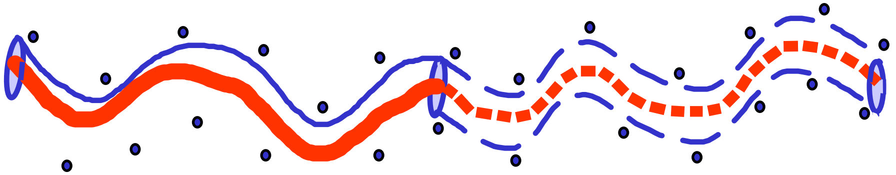
single-particle dynamics



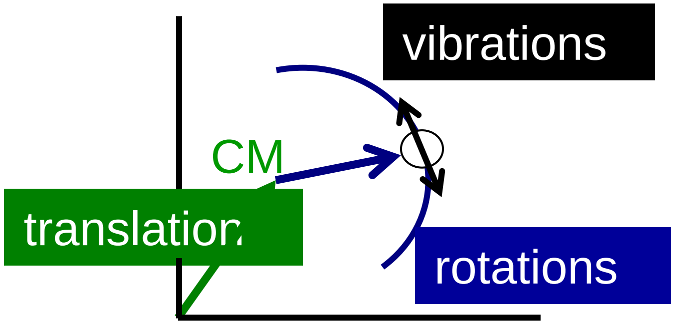
motion decomposition

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





single-particle tools



motion decomposition

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

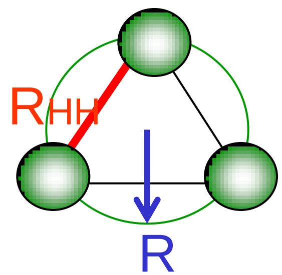
CM translation frozen for polymers T<<Tg.

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



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

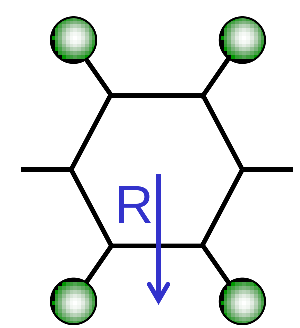
with
$$A_0(Q) = \tfrac{1}{3}\left[1+2j_0(Qr\sqrt{3})\right]$$
$$A_1(Q) = 1 - A_0(Q)$$

Phenyl proton 2-fold jumps

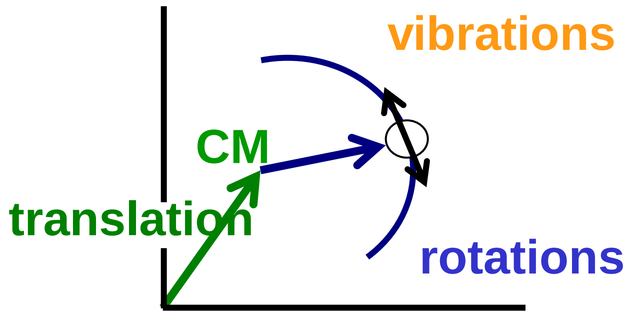
R ≈ 2.28 Å

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

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



single-particle dynamics



motion decomposition in the glass

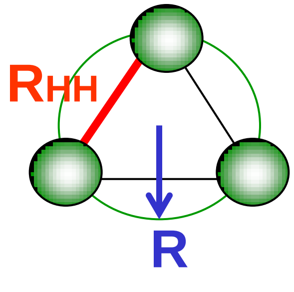
CM translation: frozen for polymers T<<Tg.

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

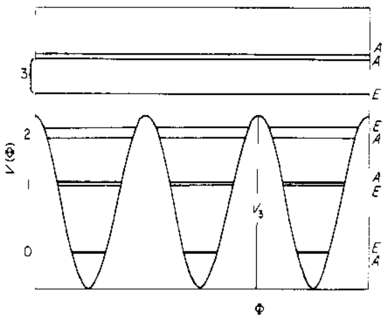
example:

Side group rotations:

Methyl protons 3-fold jumps



3-fold CH_3 potential

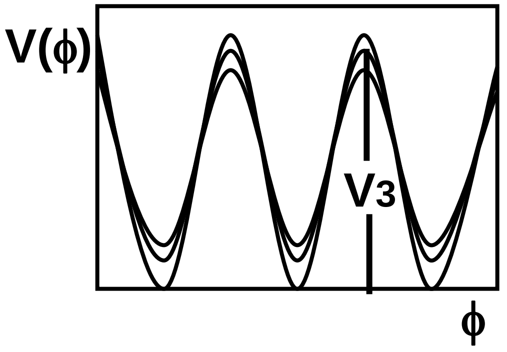


$$S_{rot}(Q,\omega) = A_0(Q)\delta(\omega) + A_1(Q)\frac{1}{\pi}\frac{3/2\tau}{(3/2\tau)^2+\omega^2}$$

with

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

distribution $\tau_{correlation}$



glassy polymers: **no single relaxation time**

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

(Gaussian) distribution of potential barriers:

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

(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

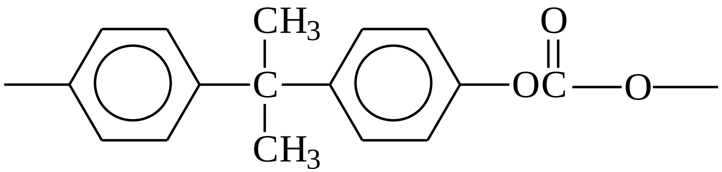
Dynamic structure factor: $S_{rot}(Q,\omega) = A_0(Q)\delta(\omega) + A_1(Q)\sum_{i=1}^{N} g_i L_i(\omega)$

Case study: Polycarbonates

Bisphenol-A polycarbonate

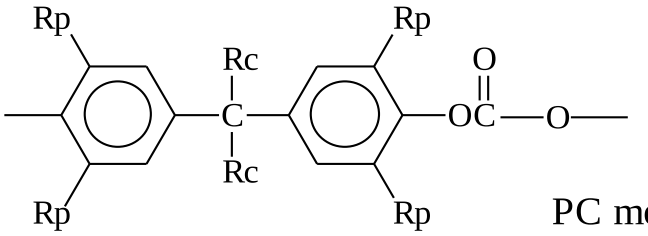
thermoplastic polymer with remarkable

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



BPA-PC

depend strongly on architecture



PC modified

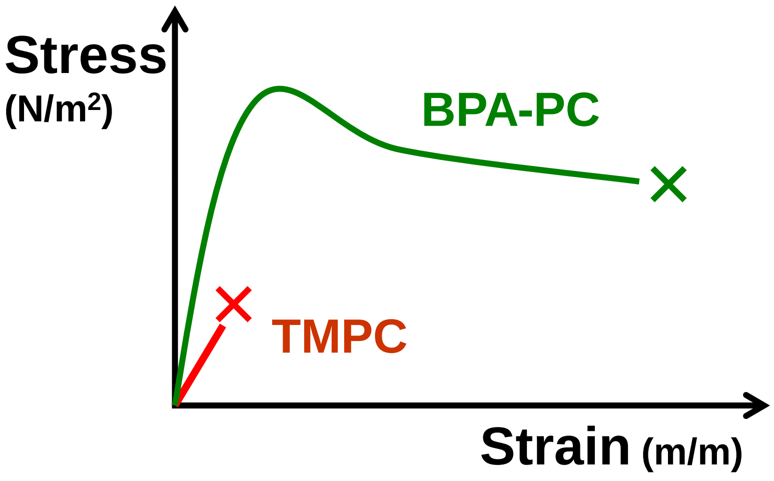
BPA-PC: ~2400 J/m

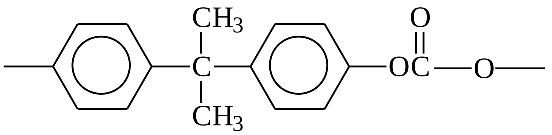
impact strength

(Fried et al. 1990)

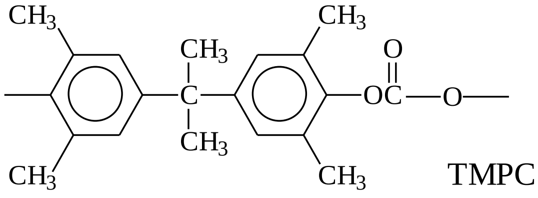
TMPC: ~70 J/m

Toughness



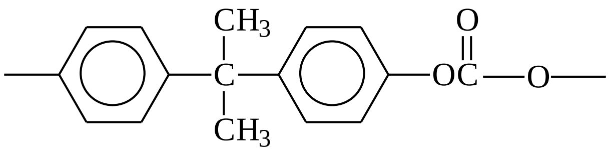


BPA-PC

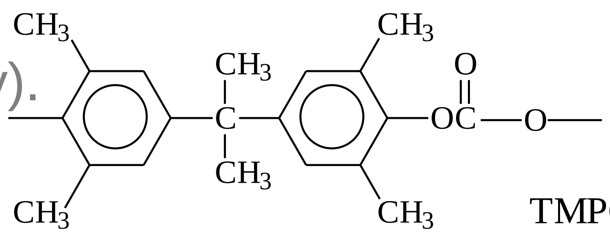


TMPC

Polycarbonates



BPA-PC



TMPC

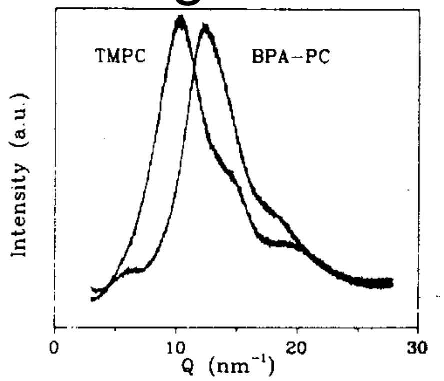
Glassy BPAPC

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

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.

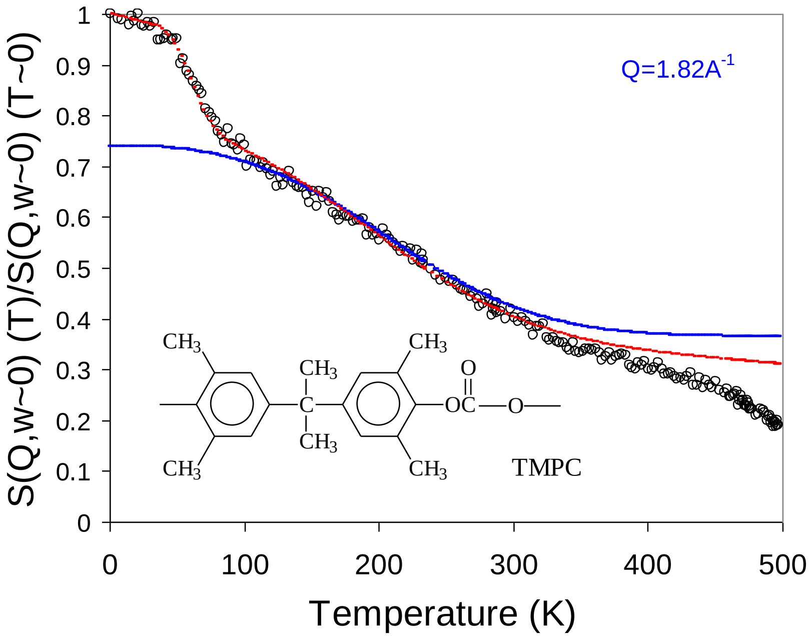
quantitative window scans

Elastic scans

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

for a Lorenztian resolution

$$S(Q,\omega \sim 0) \approx A_0(Q) + \frac{2}{\pi}[1 - A_0(Q)]\arctan\left(\frac{\Gamma_{res}}{\Gamma}\right)$$



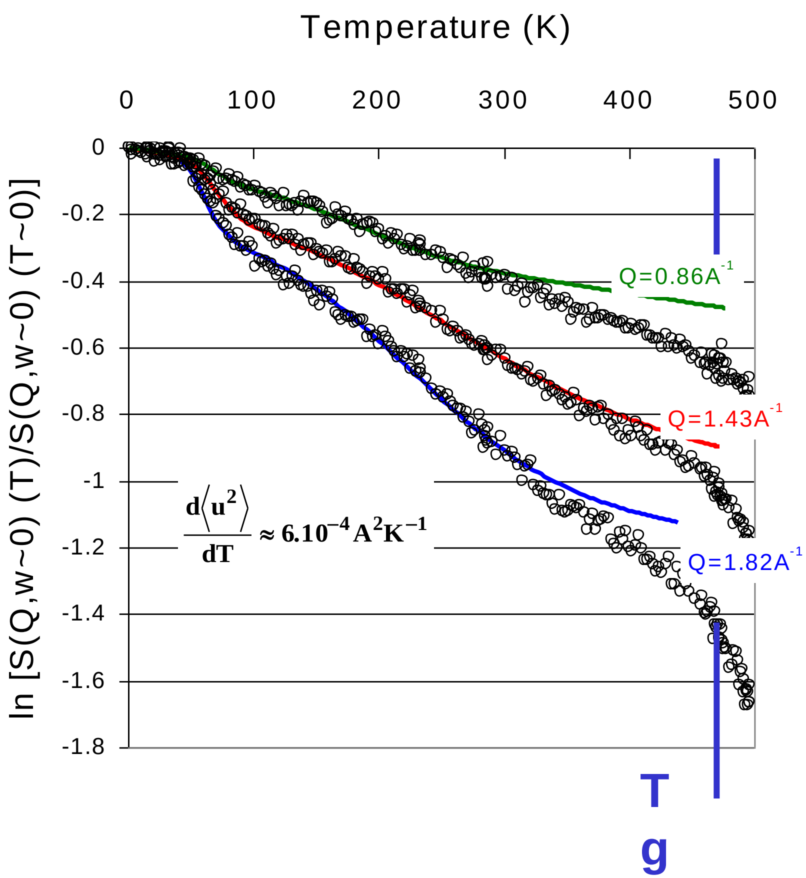
PARAMETERS

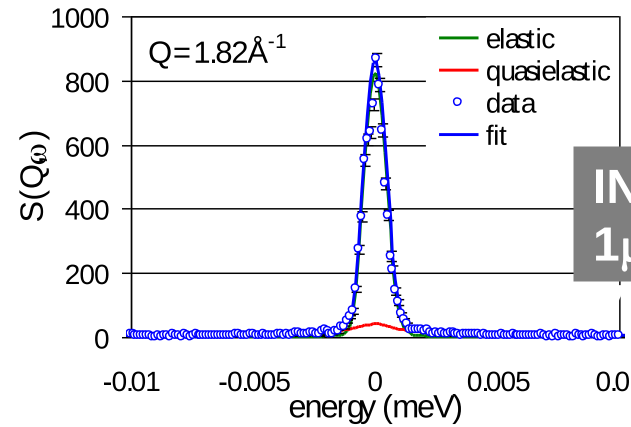
- **<u2>(T) ← initial slope**
- **distribution: E_A and σ**
- **Γo**

ASSUMED

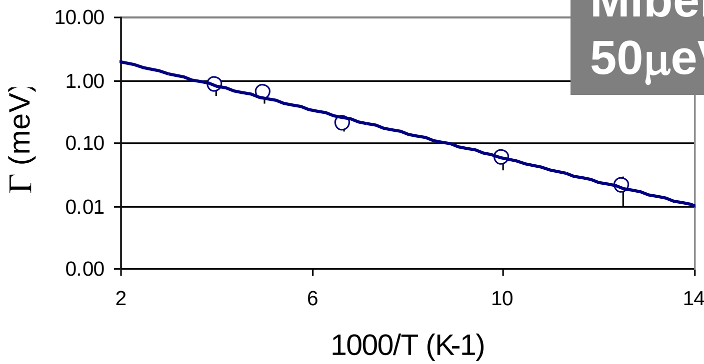
- **geometry ← EISF**
- **activation ansatz:** $\Gamma = \Gamma_0 e^{-\frac{E_A}{RT}}$

TMPC





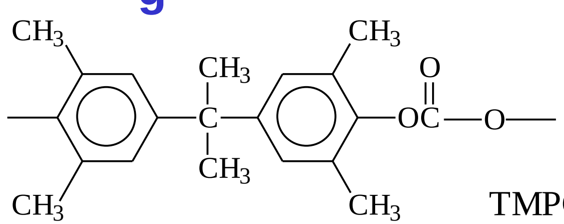
IN10 1μe



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

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

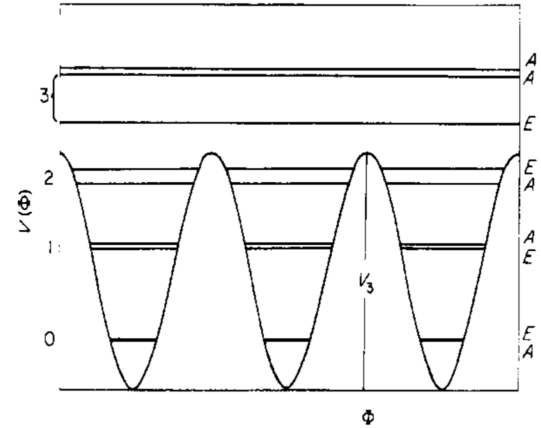
with $\hbar\omega_t \propto E_A^{3/4} e^{-\sqrt{E_A}}$

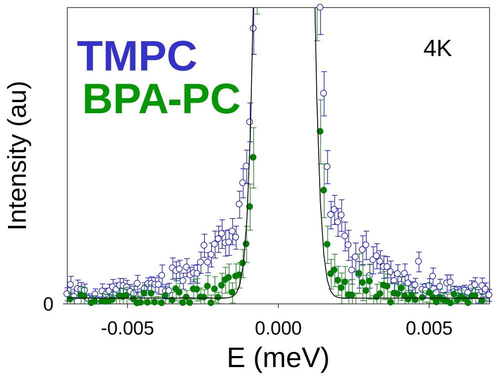
Distribution of E_A →

highly asymmetric distribution of ω_t

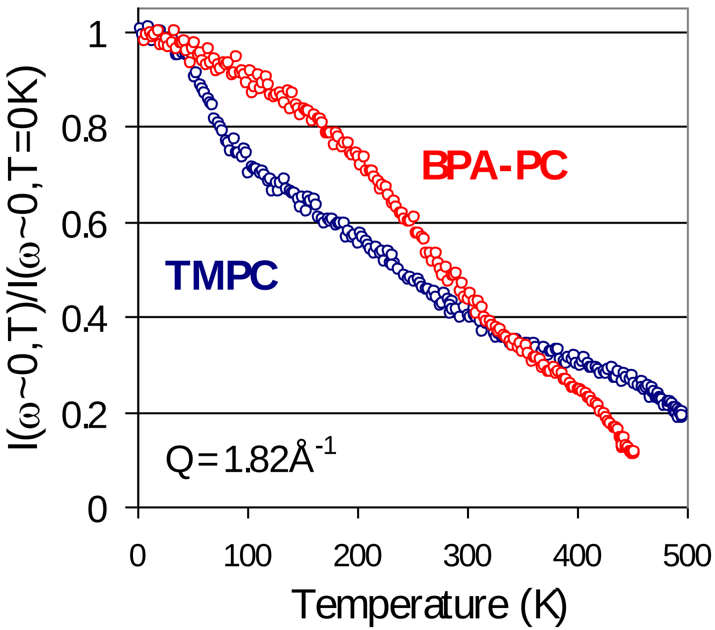
(Colmenero et al, PRL 1998)

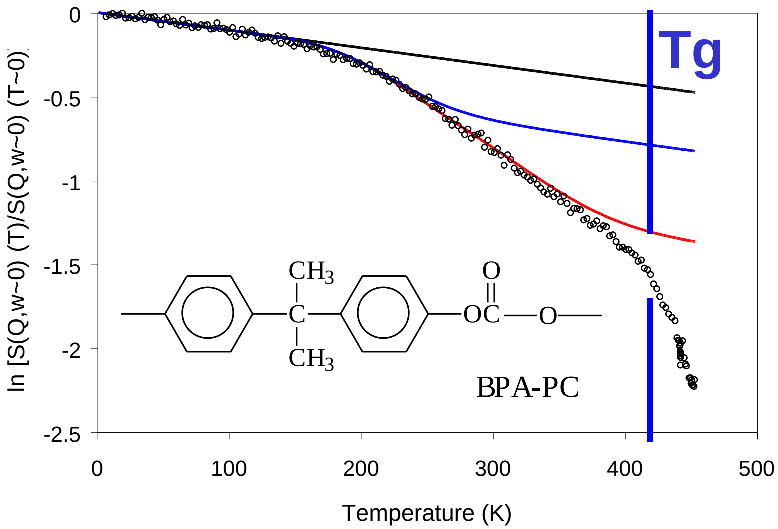
3-fold CH_3 potential

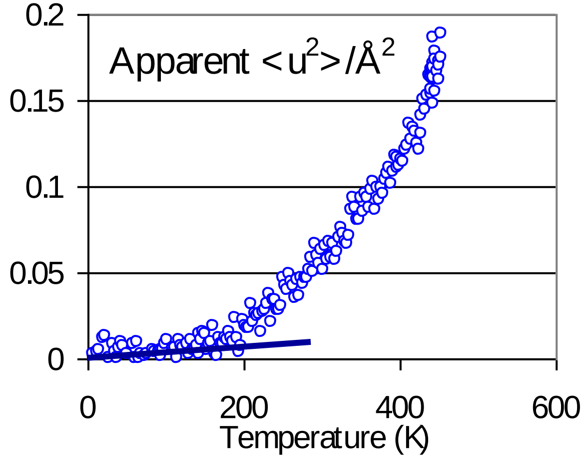




BPA-PC







Ephenyl~37 kJ/mol σ1~6

Ech3=15 kJ/mol σ1~3

compatible with TMPC

(after Spiess et al. 1987)

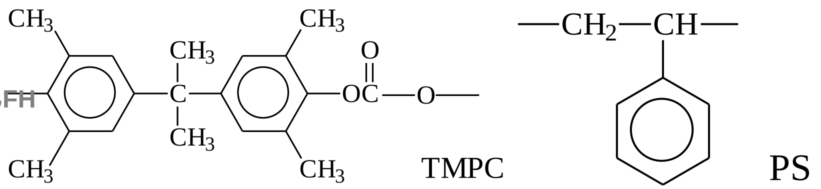
Distribution?

Glassy polymers:

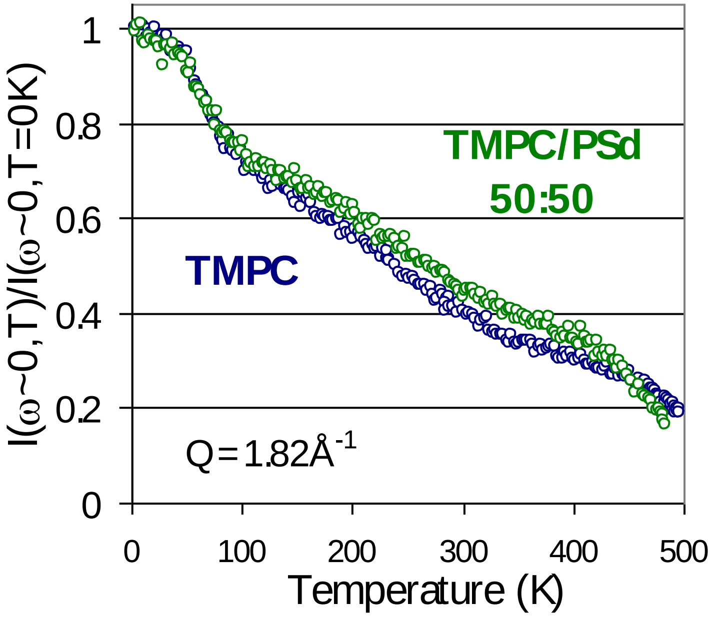
- backbone chain conformation
- Structural disorder

→ 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

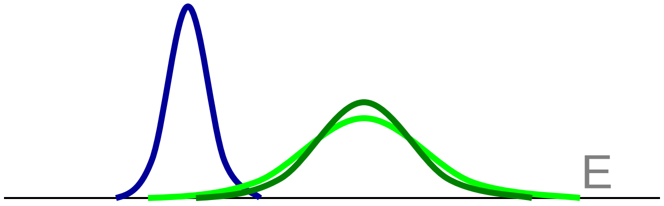
Characterisation local dynamics of PCs:

two architectures $\rightarrow$ 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